Experimental and Theoretical Investigation of the Interfacial Phenomenon Associated with Wetting of Trisiloxane Surfactant Solutions

Jovana Radulovic

A thesis submitted for the Degree of Doctor of Philosophy
The University of Edinburgh
August 2010

Declaration

I declare that this thesis has been composed by myself and is all my own work except where otherwise stated.

Jovana Radulovic

August 2010

Acknowledgements

Firstly, I would like to thank my supervisor, Dr Khellil Sefiane, for all his help and support. I was very lucky to have a supervisor who would understand my ambition and give me the freedom to explore my own ideas. His guidance and advice have been invaluable to me over the last three years.

Special acknowledgements are due to Professor Martin E. R. Shanahan, who has actively participated in my research and selflessly shared his immense scientific experience with me. His detailed comments and constructive criticism have been nothing but priceless.

There are many other people I would like to thank; without them my work would not be possible: colleagues at Scottish Microelectronic Centre, for providing the substrates and cheerful support stuff from the Workshops, who were always happy to help. I would also like to mention all the past and present members of my group, who made my PhD days more enjoyable.

Birse Foundation must be acknowledged for their generous financial support, without which none of this would have been possible.

Thanks to my family for their constant encouragement and positive energy. All my friends from King's Buildings have been great and made this a fantastic place to work for the last three years. Special thanks to those who never refused to have a c-break with me. Most of all, I want to thank Martin, who has always been reassuring, put up with all my moodiness and who always believed in me.

Abstract

Surface active agents have been successfully employed in numerous industrial, agricultural and biomedical applications for decades. Trisiloxane surfactants in particular have proved to be exceptionally effective as wetting enhancers; hence the name ‘superspreaders’. Since the early ‘90s these extraordinary surfactants have become an irreplaceable component in various products and processes. However, the true nature of their specific wetting behaviour has not been fully revealed and their underlying wetting mechanisms are still poorly understood despite substantial scientific interest during the last decades. In this thesis is an attempt to shed light on specific wetting and spreading behaviour of trisiloxane solutions.

Commercial superspreader products were tested in various environments in order to get further insight into their performance in specific practical applications. Experimental investigation of wetting of superspreader solutions on surfaces of different hydrophobicity and comparison to that of a conventional surfactant revealed superiority of trisiloxanes. Exceptional interfacial activity was explained in terms of the specific chemical structure and ‘T’-shape of the molecule. However, sensitivity of the trisiloxane head to low pH and long-time ageing in aqueous environment was revealed. Performance of binary mixtures of commercial superspreaders and conventional surfactant was also assessed. Behaviour of trisiloxanes in the capillary action was studied. Finally, a comprehensive mathematical model for trisiloxane wetting, which incorporates diffusion as the governing factor of the wetting process, was developed.

Contents

List of Papers

Paper I
On the effect of pH on spreading of surfactant solutions on hydrophobic surfaces
Radulovic, J., Sefiane, K., and Shanahan, M. E. R.
Journal of Colloid and Interface Science, Volume 332, Issue 2, 15 April 2009, Pages 497-504

Paper II
Investigation of spreading of surfactant mixtures
Radulovic, J., Sefiane, K., and Shanahan, M. E. R.
Chemical Engineering Science, Volume 64, Issue 14, 15 July 2009, Pages 3227-3235

Paper III
Spreading and Wetting Behaviour of Trisiloxanes
Radulovic, J., Sefiane, K., and Shanahan, M. E. R.
Journal of Bionic Engineering, Volume 6, Issue 4, December 2009, Pages 341-349

Paper IV
Spreading Exponents: Dynamics of Trisiloxane Wetting of Hydrophobic Surfaces
Radulovic, J., Sefiane, K., and Shanahan, M. E. R.
Defect and Diffusion Forum, 303-304 (2010) 139

Paper V
Ageing of trisiloxane solutions
Radulovic, J., Sefiane, K., and Shanahan, M. E. R.
Chemical Engineering Science, Volume 65, Issue 18, 15 September 2010, Pages 5251-5255

Paper VI
Dynamics of Trisiloxane Wetting: the Effect of Diffusion and Surface Hydrophobicity
Radulovic, J., Sefiane, K., and Shanahan, M. E. R.
J. Phys. Chem. C, **2010**, *114* (32), pp 13620–13629

List of Figures

List of Tables

Chapter 1 : Introduction

Numerous industrial (Rosen, 1987, Somasundaran and Moudgil, 1988, Wasan et al., 1988, Botsaris and Glazman, 1989, Morrow, 1990) and practical applications (Datyner, 1983, Dobias, 1993, Pugh and Bergstrom, 1994, Strechemesser and Dobias, 2005, Rudnick, 2009) are based on wetting and spreading processes. Surfactants have been frequently employed as wetting enhancers for decades. These intriguing molecules that bring together chemistry, biology, physics and engineering in the exciting field of interfacial phenomena, are nowadays commonly added to a number of products: herbicides and pesticides (Tadros, 1994, Nalewaja et al., 1998), paints and coatings (Bieleman, 2000, Florio and Miller, 2004), even in food (McClements, 2005) and drugs (Robertson and Taeusch, 1995, Lieberman et al., 1996). Understanding the complex wetting phenomena and the behaviour of different surfactant types has been proven to be crucial in designing a range of pharmaceutical (Rieger and Rhein, 1997, Rhein, 2007), chemical (Gloxhuber and Kunstler, 1992, Volkov, 2001) and bio-medical products (Elaissari, 2004, Kosaric, 1993). Although this interesting topic has been thoroughly studied for over two centuries, there are still too many unknowns in the ‘equation of wetting’, especially since the discovery of silicone surfactants (Hill, 1999, Cazabat, 1994).

Over the years many eminent scientists have investigated the everlasting and endless topic of interfacial phenomena. Since Young has placed a liquid drop on a solid surface, the search for answers and explanations has begun and still lasts even hundreds of years afterwards. The behaviour of pure liquids at interfaces has been fully revealed mostly thank to de Gennes priceless contributions. Still, modern wetting theories, which involve surfactants, are still far from the level of general knowledge. Many theoretical models have been developed in preceding decades; unfortunately most of them are applicable solely onto a particular liquid-solid system, mainly depending on the specific type of surfactants investigated. This is specifically true for trisiloxane ‘superspreaders’ which have been subjected to substantial scientific interest for years, both theoretically and experimentally. In spite of numerous research articles that have been published on this fascinating topic, no general conclusion can be drawn. On the contrary, reported conclusions may even be

interpreted as somewhat contradictory. In this thesis, I have concentrated my efforts on the problem of trisiloxane enhanced wetting of solid surfaces. I tried to shed light on the underlying mechanisms of superspreaders interfacial activity and more specifically, to determine the optimal conditions for their application.

The aspirations of my Ph.D. project were to reveal the driving force for superspreader driven wetting and to define crucial factors that affected their behaviour. Given that trisiloxanes are the main components in a few commercial products which are already in wide use worldwide, I believed my research would be more influential being based on the actual commercial trisiloxane products, rather than on highly purified trisiloxane surfactants. Although examining the key component in a commercial product may seem more demanding, especially in the sense of the interpretation of the results, I found it more rewarding as it gave me the opportunity to truly distinguish boundaries of its use. Further advantage of using commercial products in research is the possibility to have a genuine impact on people's life by adjusting the products' usage and improving the ways of its employment, yet contributing to the scientific field by revealing the underlying mechanisms for the observed phenomena. Hence, the use of the trisiloxanes and exploitation of their superspreading ability under various conditions have been optimised.

Beside practical benefits, this thesis provides theoretical contributions to the subject as well. We hoped to explain the relation between the trisiloxane molecules' atypical T-shape and its specific behaviour (Chapter 4) and to finally reveal the true nature of the superspreader's interfacial activity (Chapter 8). Attempts have been made to resolve the effects of low pH (Chapter 5) and ageing of trisiloxane solutions in aqueous environment (Chapter 6). Influence of additives in commercial products was thoroughly discussed in an extensive study about mixtures of superspreaders and conventional surfactants (Chapter 7). Superspreaders were also tested as additives for the capillary action (Chapter 9).

References 1.1

Bieleman, J. (2000) *Additives for Coatings,* Wiley-VCH, Weinheim, Germany.

Botsaris, G. D. and Glazman, Y. M. (Eds.) (1989) *Interfacial phenomena in coal technology,* Marcel Dekker.

Cazabat, F. T. a. A.-M. (1994) *EPL (Europhysics Letters),* **25,** 205.

Datyner, A. (Ed.) (1983) *Surfactants in textile processing,* Marcel Dekker.

Dobias, B. (Ed.) (1993) *Coagulation and flocculation : theory and applications,* Marcel Dekker.

Elaissari, A. (Ed.) (2004) *Colloidal biomolecules, biomaterials, and biomedical applications* Marcel Dekker.

Florio, J. J. and Miller, D. J. (2004) *Handbook of Coatings Additives,* Marcel Dekker, New York, USA.

Gloxhuber, C. and Kunstler, K. (Eds.) (1992) *Anionic surfactants : biochemistry, toxicology, dermatology,* Marcel Dekker.

Hill, R. M. (Ed.) (1999) *Silicone Surfactants,* Marcel Dekker.

Kosaric, N. (Ed.) (1993) *Biosurfactants : production, properties, applications,* Marcel Dekker.

Lieberman, H. A., Rieger, M. M. and Banker, G. S. (1996) *Pharmaceutical dosage forms-disperse systems,* Marcel Dekker, New York.

McClements, D. J. (2005) *Food emulsions: principles, practices and techniques,* CRC Press.

Morrow, N. R. (Ed.) (1990) *Interfacial phenomena in petroleum recovery,* Marcel Dekker.

Nalewaja, J. D., Goss, G. R. and Tann, R. S. (Eds.) (1998) *Pesticide formulations and application systems,* Philadelphia.

Pugh, R. J. and Bergstrom, L. (Eds.) (1994) *Surface and colloid chemistry in advanced ceramics processing,* Marcel Dekker.

Rhein, L. D. (Ed.) (2007) *Surfactants in personal care products and decorative cosmetics,* CRC Press, Taylor & Francis.

Rieger, M. M. and Rhein, L. D. (Eds.) (1997) *Surfactants in cosmetics,* Marcel Dekker.

Robertson, B. and Taeusch, H. W. (Eds.) (1995) *Surfactant therapy for lung disease,* Marcel Dekker, New York.

Rosen, M. J. (Ed.) (1987) *Surfactants in emerging technologies,* Marcel Dekker.

Rudnick, L. R. (2009) *Lubricant Additives: Chemistry and Applications,* CRC Press, Taylor & Francis Group.

Somasundaran, P. and Moudgil, B. M. (Eds.) (1988) *Reagents in mineral technology,* Marcel Dekker.

Strechemesser, H. and Dobias, B. (Eds.) (2005) *Coagulation and Flocculation: Theory and Applications,* CRC Press, Taylor & Francis.

Tadros, T. F. (Ed.) (1994) *Surfactants in agrochemicals,* Marcel Dekker.

Volkov, A. G. (Ed.) (2001) *Liquid interfaces in chemical, biological, and pharmaceutical applications,* Marcel Dekker.

Wasan, D. T., Ginn, M. E. and Shah, D. O. (Eds.) (1988) *Surfactants in chemical/process engineering,* Marcel Dekker.

Chapter 2 : Wetting and Spreading of Surfactant Solutions

2.1 Fundamentals of Wetting

When a liquid is in contact with the solid or another liquid it is said the liquid wets the solid, or another liquid. In this thesis only wetting of solids by liquids are considered. When a small liquid drop is placed onto the solid surface, it will wet the surface until equilibrium is reached. The extent of wetting observed is the consequence of the balance of forces that act on the three-phase (*l*-*s*-*g*) contact line, the so-called triple line. The wetting process is characterised by the change in shape of the drop and, consequently, its geometrical parameters. Once equilibrium, which may be defined as the state with the minimal excess of the total free energy of the system, is reached, the shape of the drop stops varying and wetting parameters are no longer changing. The constancy of the equilibrium contact angle (θ_{eq}) of a liquid drop on a solid surface as a function of the surface free energy, the interfacial free energy and the surface tension of the liquid was first introduced by Young (1804). In years to come Dupré incorporated thermodynamic effects and nowadays this relationship is very well-known and widely used Young–Dupré equation:

$$\cos\theta_{eq} = \frac{\gamma_{sg} - \gamma_{sl}}{\gamma_{\mathrm{lg}}} \tag{2.1}$$

where γ_{sg}, γ_{sl} and γ_{lg} are interfacial tensions at solid-gas, solid-liquid and liquid-gas interfaces, respectively (Figure 2.1).

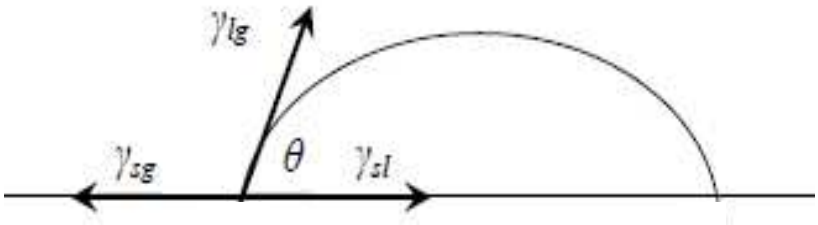


Figure 2.1 Liquid drop in contact with a solid surface. The equilibrium contact angle, θ_{eq}, is the consequence of three tension forces acting.

Young-Dupré equation is based on the equilibrium thermodynamics of the ideal system and is therefore restricted by the following assumptions:

- Gravity and line tension contributions can be neglected
- Inert and flat solid surface
- All three interfacial tensions are not changing.

The surface energy is one of the basic properties of a solid surface and varies greatly for different materials. Value of the surface energy is the consequence of the type and the intensity of the intermolecular forces acting inside the solid. General rule is that liquids with surface tension lower than the surface energy of the solid wet the substrate. Most metals and surfaces similar to silica have high surface energies and are therefore wetted by most liquids (Isrealchvilli, 1991). On the other hand, polymers and waxes have low surface energies (Brandrup et al., 1999) and to what extent a liquid will wet low-energy surface primarily depends on the surface tension of the liquid. Hydrophobicity of the substrate is usually characterised in terms of the contact angle pure water drop exhibits on the particular surface. When a drop is brought in contact with the solid surface, depending on its free energy, three wetting scenarios may occur. Complete wetting (Figure 2.2) happens in case when liquid drop spreads over the surface with contact angle progressively decreasing to very low values. Otherwise, a drop forms a finite contact angle with the surface. If the contact angle is between 0° and 90° partial wetting takes place (Figure 2.3). Values of the contact angle bigger than 90° indicate non-wetting (Figure 2.4) and corresponding surfaces are referred to as hydrophobic.

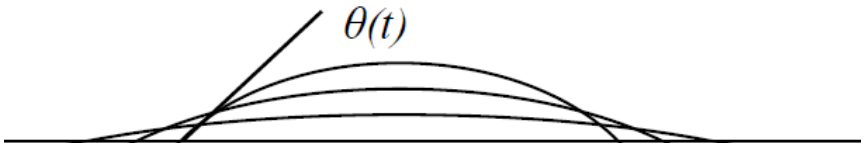


Figure 2.2 Complete wetting; spreading of the liquid drop.

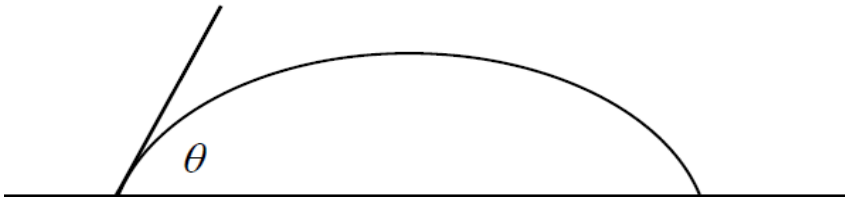


Figure 2.3 Partial wetting ($0° < \theta < 90°$).

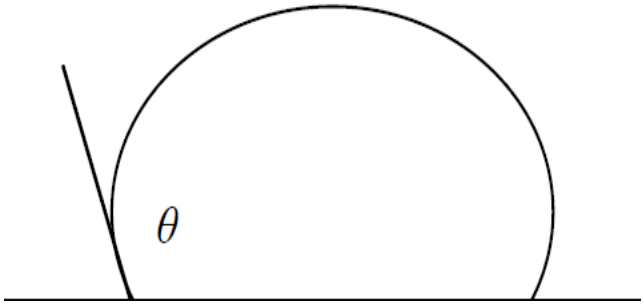


Figure 2.4 Non-wetting ($\theta > 90°$).

2.2 Theories behind Wetting

When a liquid drop is placed onto a flat surface, capillary forces drive the interface spontaneously towards the equilibrium. At the same time, there is the hydrodynamic resistance to spreading that opposes the capillary driving force. Evolutions of the drop radius and the contact angle with time are commonly investigated to describe the dynamics of wetting on solid surfaces. For pure liquids two dissimilar theoretical approaches have been developed to describe spreading of the drop: the hydrodynamic model (Cox, 1986, Hoffmann, 1975, Voinov, 1976, Tanner, 1979, Dussan and Davis, 1974) and the molecular-kinetic model (Blake et al., 1997, Hayes and Ralston, 1994, Lin et al., 1981). The main difference between these two descriptions is the dominant energy dissipation channel during the drop shape transformation. The dissipation of energy in the hydrodynamic model is due to the viscous drag within the spreading droplet, unlike the molecular-kinetic model where the dissipation of energy is caused by friction at the three-phase contact line (intermolecular interactions between the solid and the liquid). De Gennes and Brochard-Wyart concluded hydrodynamics is essential for low angles, while

molecular features are important at high velocities and large angles (Brochard-Wyart and de Gennes, 1992). Other authors showed that hydrodynamic model successfully describes complete wetting for viscous systems, while molecular-kinetic model is more appropriate for partial wetting (De Ruijter et al., 1997).

It has been shown that the hydrodynamic regime may be characterized asymptotically by the tendency of drop radius and contact angle to follow the power law:

$$R \sim t^{\frac{1}{10}} \tag{2.2}$$

$$\theta \sim t^{\frac{3}{10}} \tag{2.3},$$

while the molecular-kinetic model leads to different time scales:

$$R \sim t^{\frac{1}{7}} \tag{2.4}$$

$$\theta \sim t^{\frac{3}{7}} \tag{2.5}.$$

In recent publications (De Ruijter et al., 1999, De Ruijter et al., 2000) a combined model was presented to describe the dynamics of a spreading drop, allowing dissipation in both channels: friction against the substrate and the hydrodynamic effects. This approach allowed identifying several stages in the wetting process: a fast early-time stage characterized by a linear time-dependence of the base radius, followed by a kinetic stage, which can be successfully modelled by molecular-kinetic and subsequently hydrodynamic model, and finally an exponential relaxation to the equilibrium state. All the models described above proved to be a powerful tool for portrayal of wetting behaviour of pure liquids. Nevertheless, none of them gave satisfactory fit for wetting with surfactants solutions.

2.3 Surfactant Solutions

Surfactants (*surf*ace *act*ive *a*g*ents*) are amphiphilic molecules which consist of hydrophilic (polar) and hydrophobic (non-polar) parts. In common surfactants, polar part of the molecule is usually denoted as the head-group and the non-polar part is the tail. Depending on the nature of the head group, surfactant molecules can be characterised as ionic (anionic, cationic, zwitterionic) or nonionic. In this thesis, effort has been concentrated on studying different types of nonionic surfactants. Moreover, investigated surfactant types have specific chemical structure: hydrophilic tail and hydrophobic head group - the opposite of common surfactant types. Surfactants studied have polar (hydrophilic) tails that consist of polyethylene oxide segments of different lengths, while the head-groups of different surfactants have dissimilar properties, which is discussed in more details in Chapter 3.

Addition of surfactant can transform a non-wetting aqueous solution into a wetting solution even on hydrophobic substrates. The term wetting agent is applied to any substance that increases the ability of water or an aqueous solution to wet a solid surface. Altering the wetting ability of water is an important property shown to some degree by all surfactants, although the extent to which they exhibit this phenomenon varies greatly. Due to their dual nature surfactants tend to pack into interfaces between polar and non-polar regions, lowering the free energy of the system. It is often said surfactants favour the expansion of the interface by lowering the surface tension of the liquid. Additionally, micellisation takes place as an alternative mechanism for decreasing the interfacial energy of a surfactant solution by arranging molecules into energetically favourable aggregates. Here we introduce CMC (*c*ritical *m*icelle *c*oncentration) as main parameter of a surfactant solution. Below CMC, surfactant molecules are freely solubilised in the solution; above CMC, spontaneous aggregation takes place. Structure of surfactant aggregates mostly depends on the nature and type of the surfactant, but also on the properties of the solvent surfactant is dispersed in. Isrealachvili (Isrealchvilli, 1991) showed that geometrical factors

dictate the aggregate structure and introduced the surfactant parameter, N_S, (packing ratio) as the most convenient parameter for prediction of the aggregate structure:

$$N_S = \frac{V}{la_o} \tag{2.6}$$

where V is volume of the hydrophobic part (in common surfactants, the tail), a_o is the area of the surfactant head group and l is the length of the tail. Estimation of these geometrical parameters may be challenging, since the area of the surfactant head and especially the length of the tail are influenced by the type of interactions with the solvent molecules, surfactant concentration and other environmental factors (Myers, 2006). Very small values of N_S indicate spherical or ellipsoidal micelles; for values of N_S close to unity vesicles and bilayer structures are expected. When N_S is above 1 inverted micelles are formed (Nagarajan, 2002). Alternatively, hydrophilic-lipophilic balance (HLB) can be used as an additional parameter for evaluation of solubility of non-ionic surfactant and its interfacial properties. HLB is the ratio between hydrophilic and lipophilic potion of a non-ionic surfactant molecule and it is generally used for estimation of the expected emulsification performance.

2.4 Influence of Surfactants on Wetting

Due to their immense importance in numerous practical and industrial applications, enhanced wetting with surfactant solutions has been subjected to considerable research interest over the past decades. Scales et al. (Scales et al., 1986) were one of the first to point out the importance of the nature of the solid substrate in the wetting process. They introduced characteristic normalisation of the wetting behaviour as a powerful tool to give both a qualitative and quantitative understanding of adsorption of a series of alkyl aryl polyoxyethylenes. Significance of the substrate hydrophobicity was also exposed by Keurentjes et al. (Keurentjes et al., 1990). They have determined that a surfactant, when adsorbed onto the hydrophobic solid, exposes its polar head groups to the solution, whereas in the case of the hydrophilic

solid a by-layer of surfactants may form. Eriksson et al. (Eriksson et al., 2001) gave further understanding why surfactant transfer to three-phase contact line is dominant process in wetting. Ever since transfer of surfactant molecules to the interface is believed to dictate the overall dynamics of wetting and many attempts to quantify this phenomenon have been made.

Over the years various wetting and spreading regimes have been revealed and recognised depending on the type of the investigated liquid-solid system. One of the most comprehensive studies on dynamic wetting of surfactant solutions, and relevant factors that may influence the wetting process, was done by Joos et al. (Joos et al., 1999). Von Bahr (von Bahr et al., 2001) reported two wetting stages at low surfactant concentrations: a short time regime where spreading occurs rapidly and a long time regime where spreading is slow. This was confirmed by Dutschk et al. (Dutschk et al., 2003) who investigated wetting behaviour of dilute ionic and nonionic aqueous surfactant solutions over highly hydrophobic and moderately hydrophobic polymer surfaces. They found that nonionic surfactants enhanced spreading in both type of surfaces, whereas ionic surfactants do not spread over highly hydrophobic surfaces. However, they argued the long time regime goes much slower and concluded a possible explanation is that adsorption at the expanding solid-liquid interface goes more slowly than the diffusion. Lee et al. (Lee and Starov, 2007, Lee and Starov, 2009) verified the existence of two wetting stages by investigating the effect of surfactant solubility. At all concentrations above CMC and for all types of inspected surfactants wetting considerably depended on the solubility of surfactants: the higher solubility, the slower spreading. Von Bahr (von Bahr et al., 1999) has also noticed that presence of micelles significantly slows the surfactant transport, and consequently spreading on the whole. Lee et al. (Lee and Starov, 2007) observed that high solubility in aqueous solutions, typical of ionic surfactants: SDS and DTAB, slows down both the first and the second stage; if the solubility is high enough then during the second stage the front reaches some final position and does not move any further. Low soluble nonionic surfactants (Tween® 20, Tergitol® NP10) showed faster wetting during both stages and observed dynamics was successfully modelled by a power law, $R(t) = const \cdot t^n$, where n is the spreading exponent.

Chan and Borhan (Chan and Borhan, 2005) deduced that insoluble monolayer enhances the overall spreading rate. They developed mathematical model for surfactant enhanced spreading that suggests two additional mechanisms that influence the spreading rate: the development of positive surface curvature near the moving contact line, which produces a favourable radial pressure gradient within the drop and the surfactant convection in a vicinity of the moving contact line. Accumulation of the surfactant at the contact line, due to surface convection, leads to faster spreading of a drop. On the other hand, Starov et al. (Starov et al., 2000) described the spreading mechanism of aqueous surfactant solutions over hydrophobic surfaces as a transfer of surfactant molecules on the bare hydrophobic surfaces in front of the moving liquid on the three-phase contact line. This mechanism was first mentioned elsewhere (Churaev and Zorin, 1995, Zolotarev et al., 1976, Churaev et al., 1981); in (Starov et al., 2000) authors broadened the idea assuming surfactant transfer to the droplet front to be the rate-determining step and the drop surface coverage as an increasing function of the bulk surfactant concentration inside the drop, whose maximum is reached close to the CMC.

2.5 Superspreading

Silicone surfactants have drawn significant attention in the past decades. Due to their exceptional wetting abilities trisiloxanes, in particular, have been subjected to substantial interest recently. Trisiloxane surfactants (Figure 2.5) are commonly denoted as M(D´EO_nR)M, where M represents the trimethylsiloxy group, M=$(CH_3)_3$-SiO–, the term D´=–Si(CH_3)(R')–, where R'=$(CH_2)_3$ onto which is polyoxyethylene group, EO_n=$(CH_2CH_2O)_n$, attached, with *n* as the average number of polyoxyethylene groups, and R stands for an end-capping group, usually –H, –CH_3, or –Ac; Ac=–C(O)CH_3. Until recently trisiloxane with eight poly(oxyethylene) groups was generally referred to as E_8. However, a large selection of commercial trisiloxane products is available on the world market nowadays and these will be called correspondingly by their registered trade names (see Chapter 3).

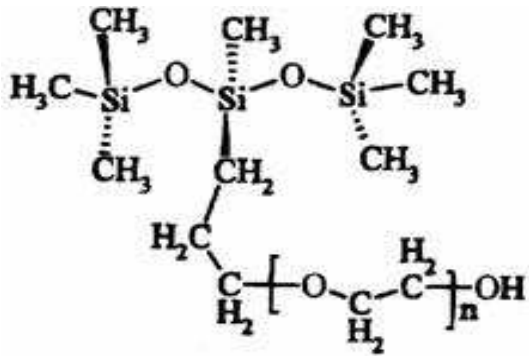


Figure 2.5 Trisiloxane ‘superspreader’ molecule.

Trisiloxanes possess an unusual ability to induce highly efficient wetting properties even on hydrophobic surfaces. It has been reported that the addition of trisiloxane surfactants can transform a small spherical drop into ‘infinitely’ thin liquid film – the phenomenon popularly known as ‘superspreading’ (Hill, 2002, Hill, 1998, Hill, 1999). Thus, trisiloxane surfactants are widely recognized as ‘the superspreaders’. Due to its unique characteristics and the colossal practical employment, the superspreading phenomenon has attracted much attention, especially from the theoretical point of view. In spite of considerable research interest, there is still a lack of explanation of the underlying mechanism of superspreaders’ behaviour and understanding of the necessary conditions for its realisation. Superiority of trisiloxanes has been confirmed in numerous publications over the years (Nikolov et al., 2002, Hill, 1998, Ananthapadmanabhan et al., 1990, Stoebe et al., 1997, Svitova et al., 1996, Hill, 1999, Hill, 2002). It is believed that the overall wetted area achievable by an aqueous droplet containing trisiloxane surfactant can be as much as 50 times greater than pure water, and 25 times more effective than a conventional surfactant (Nikolov et al., 2002). Nevertheless, researchers still disagree about the nature of the driving force and interpretation of the observed dynamics.

Rafai and Bonn (Rafai and Bonn, 2005, Rafai et al., 2002) suggested $R \propto t^n$ power law to describe trisiloxane spreading, with power n larger than 0.1 for concentrations both above and below CMC. For very high bulk concentrations linear relation $R \propto t$ was obtained. Svitova et al. (Svitova et al., 1996, Svitova et al., 1998, Svitova et al., 2001) introduced additional parameters: the critical wetting concentration (CWC),

which they claimed to be independent of the substrate surface energy, and the critical aggregation concentration, CAC; the later being very similar to CMC. Only very high concentrations (several times CAC) of trisiloxanes were reported as the necessary condition for superspreading on hydrophobic surfaces (Svitova et al., 1996, Svitova et al., 1998). In (Svitova et al., 2001) three regimes of the spreading dynamics were observed: early stages where wetting diameter is proportional to t^n with n in the range 0.12 – 0.22; during the second stage the exponent increases to 0.38 – 0.58; during the last stage of spreading the surface roughness and local tension gradients lead to asymmetric drop shape and formation of fingers and dendrites. Nikolov et al. (Nikolov et al., 2002) also reported finger instabilities during spreading of the drop of aqueous Silwet L-77® solution on a hydrophobic plate. Stoebe et al. (Stoebe et al., 1996) observed the small fingers appeared at the edges of droplets of aqueous trisiloxane solutions but found the length of fingers was less than 10 % of the dynamic droplet radius, which served as a reason not to consider the fingering in the analysis of their experiment. Recently Starov et al. (Ivanova et al., 2009) compared kinetics of spreading of conventional nonionic surfactants to that of trisiloxanes. Three regimes of spreading have been identified (i) complete non-wetting during the spreading process at low concentrations, (ii) a transition from initial non-wetting to partial wetting at the end of the spreading process at intermediate concentrations, and (iii) partial wetting both at the beginning and the end of the spreading process at higher concentrations and related transitions between different regimes to relevant critical concentrations: CAC or CMC, and CWC, which have also been precisely determined (Ivanova et al., 2010).

Initial attempts to shed light on trisiloxane's wetting ability were related to its ability to adsorb at the interface and significantly reduce tensions at the moving liquid front, creating a positive spreading coefficient. However, the positive value of the spreading coefficient during spreading could not be either proved or theoretically explained, because the adsorption cannot keep pace with the expansion of the drop due to diluted solutions at the perimeter and the surface concentrations becomes reduced at the contact line. The main drawback of latter explanation is that it can be equally applied to any aqueous surfactant solution and unfortunately is not specific

for trisiloxanes. Subsequent theories included the presence of disperse phase as a vital parameter in superspreading. Ruckenstein (Ruckenstein, 1996) assumed multilayer adsorption is a possible reason for fast spreading to occur. Svitova et. al. (Svitova et al., 2001) gave further insight into surfactant self-assembly and aggregate structure as main factor responsible for transition between partial to complete wetting. Zhu et al. (Zhu et al., 1994) confirmed superspreading occurs only when dispersed particles (vesicles) are present. It was concluded in (He et al., 1993, Hill et al., 1994) that in the range of 0.01 – 0.025 wt %, trisiloxane solutions contain vesicles. However, Nikolov et al. (Nikolov et al., 2002) suggested that although aggregates are present in the solution, they do not play a crucial role in initiating the Marangoni effect. Kumar et al. (Kumar et al., 2003) pointed out that bilayer adsorption may account for the ability of superspreaders to maintain the low apex concentration necessary to drive Marangoni spreading, or a high concentration at the contact line to maintain a low contact angle and force spreading.

Modern hypothesis for the explanation of the superspreading phenomenon vastly differ. A number of theories are based on the formation of a precursor film on a solid surface (Stoebe et al., 1996). Zhu et al. (Zhu et al., 1994) noted the influence of the water vapour pressure in the surrounding atmosphere on the trisiloxane wetting as superspreading was observed only in saturated or supersaturated water vapour. This has given rise to the suggestion that fast spreading may be caused by surface flow of a thin precursor film formed from the vapour phase. Churaev et al. (Churaev et al., 2001) showed that fast spreading and climbing of trisiloxane surfactant solutions over hydrophobic surfaces, are caused by formation of extremely thick wetting films of the solution and introduced the important role of disjoining pressure. Marangoni mechanism is also believed to contribute to the rapid spreading: the surface concentrations at the drop apex are assumed to remain high as compared to the perimeter so that the drop is pulled out by the higher tension at the perimeter than at the apex. To maintain a high apex concentration, surfactant adsorption must exceed the rate of interfacial dilation at the apex due to the outward flow. Nikolov and Wasan (Nikolov et al., 2002, Chengara et al., 2002) provided considerable evidence of surface tension gradient being an important driving force in superspreading.

Stoebe et al. (Stoebe et al., 1997) fused the above hypothesis claiming aggregate disintegration plays an important part as it results in sudden increases in surface tension gradients and a corresponding increase in Marangoni flow.

Ananthapadmanabhan et al. (Ananthapadmanabhan et al., 1990) postulated that the rapid spreading is a consequence of the unusual shape of the hydrophobe group. Kumar et al. (Kumar et al., 2003) compared superspreaders to *n*-alkyl polyoxyethylene surfactants, which have *n*-alkyl chain instead of trisiloxane backbone. Hydrophobicity of alkyl chain and the trisiloxane backbone is approximately the same, but their size is very different, which they believed to be one of main reasons for different spreading power of polyethoxylates with alkyl groups and trisiloxanes. However, Hill claimed that 'T' ('umbrella-like') shape of superspreader molecule is not the explanation of unusual wetting properties and emphasised the importance of the end-capping groups (Hill, 2002, Hill, 1999, Hill, 1998). Svitova et al. (Svitova et al., 1996) generally concluded that the rate of spreading depends on surfactant nature, structure (hydrophobicity), concentration and the subphase nature. The increase of surfactant hydrophobicity (ethoxy chain length) suppresses the superspreading ability of siloxane (and apparently hydrocarbon) surfactants. Njobuenwu (Njobuenwu, 2007) noticed that water droplets containing trisiloxanes with short chain lengths in most of the experiments did not spread at all.

The most recent investigation approaches include infrared spectroscopy studies (Kumar et al., 2006) and molecular dynamics simulations (Halverson et al., 2009). Although these methods have given certain fresh insight into trisiloxane behaviour, the overall results are not too promising. Additionally, the number and the nature of surfaces wetting of trisiloxanes has been tested on is very limited. Early experiments were conducted on Parafilm (Hill, 1998, Zhu et al., 1994, Stoebe et al., 1996), but over the years different polymer surfaces with varying hydrophobicity and roughness dominated, although spreading was investigated on more unusual substrates like graphite (Svitova et al., 2001), mineral oil (Stoebe et al., 1997) or hydrocarbons (Svitova et al., 1996), as well as on cabbage (*Brasslca oleracea*) and wheat (*Triticum*

aestivum L.) leaves (Zhang et al., 2006), lotus (Tang et al., 2008) and velvetleaf (*Abutilion theophrasti*) (Chengara et al., 2002, Nikolov et al., 2002). Nevertheless, there is still a lot of investigation yet to be done for variety of superspreaders-hydrophobic substrate systems until complete understanding of these phenomena is achieved.

2.6 References

Ananthapadmanabhan, K. P., Goddard, E. D. and Chandar, P. (1990) *Colloids and Surfaces,* **44,** 281-297.

Blake, T. D., Clarke, A., De Coninck, J. and de Ruijter, M. J. (1997) *Langmuir,* **13,** 2164-2166.

Brandrup, J., Immergut, E. H., Grulke, E. A., Abe, A. and Bloch, D. R. (1999) *Polymer Handbook,* John Wiley & Sons, Inc, New York.

Brochard-Wyart, F. and de Gennes, P. G. (1992) *Advances in Colloid and Interface Science,* **39,** 1-11.

Chan, K. Y. and Borhan, A. (2005) *Journal of Colloid and Interface Science,* **287,** 233-248.

Chengara, A., Nikolov, A. and Wasan, D. (2002) *Colloids and Surfaces A: Physicochemical and Engineering Aspects,* **206,** 31-39.

Churaev, N. V., Esipova, N. E., Hill, R. M., Sobolev, V. D., Starov, V. M. and Zorin, Z. M. (2001) *Langmuir,* **17,** 1338-1348.

Churaev, N. V., Martynov, G. A., Starov, V. M. and Zorin, Z. M. (1981) *Colloid & Ploymer Sci,* **259,** 747-752.

Churaev, N. V. and Zorin, Z. M. (1995) *Colloids and Surfaces A: Physicochemical and Engineering Aspects,* **100,** 131-138.

Cox, R. G. (1986) *J. Fluid Mech.,* **168,** 194-220.

De Ruijter, M. J., Charlot, M., Voué, M. and De Coninck, J. (2000) *Langmuir,* **16,** 2363-2368.

De Ruijter, M. J., De Coninck, J., Blake, T. D., Clarke, A. and Rankin, A. (1997) *Langmuir,* **13,** 7293-7298.

De Ruijter, M. J., De Coninck, J. and Oshanin, G. (1999) *Langmuir,* **15,** 2209-2216.

Dussan, E. B. V. and Davis, S. H. (1974) *Journal of Fluid Mechanics,* **65,** 71-95.

Dutschk, V., Sabbatovskiy, K. G., Stolz, M., Grundke, K. and Rudoy, V. M. (2003) *Journal of Colloid and Interface Science,* **267,** 456-462.

Eriksson, J., Tiberg, F. and Zhmud, B. (2001) *Langmuir,* **17,** 7274-7279.

Halverson, J. D., Maldarelli, C., Couzis, A. and Koplik, J. (2009) *Chemical Engineering Science,* **64,** 4657-4667.

Hayes, R. A. and Ralston, J. (1994) *Langmuir,* **10,** 340-342.

He, M., Hill, R. M., Lin, Z., Scriven, L. E. and Davis, H. T. (1993) *J. Phys. Chem.,* **97,** 8820-8834.

Hill, R. M. (1998) *Current Opinion in Colloid & Interface Science,* **3,** 247-254.

Hill, R. M. (Ed.) (1999) *Silicone Surfactants,* Marcel Dekker.

Hill, R. M. (2002) *Current Opinion in Colloid & Interface Science,* **7,** 255-261.

Hill, R. M., He, M., Davis, H. T. and Scriven, L. E. (1994) *Langmuir,* **10,** 1724-1734.

Hoffmann, R. L. (1975) *J. Colloid Interface Sci.,* **50,** 228-241

Isrealchvilli, J. (1991) *Intermolecular and Surface Forces,* Academic Press, San Diego.

Ivanova, N., Starov, V., Johnson, D., Hilal, N. and Rubio, R. (2009) *Langmuir,* **25,** 3564-3570.

Ivanova, N., Starov, V., Rubio, R., Ritacco, H., Hilal, N. and Johnson, D. (2010) *Colloids and Surfaces A: Physicochemical and Engineering Aspects,* **354,** 143-148.

Joos, P., Fainerman, V. B., Loglio, G., Lucassen-Reynders, E. H., Miller, R. and Petrov, P. (1999) *Dynamic Surface Phenomena,* VSP Books, Utrecht.

Keurentjes, J. T. F., Cohen Stuart, M. A., Brinkman, D., Schroen, C. G. P. H. and van Riet, K. (1990) *Colloids and Surfaces,* **51,** 189-205.

Kumar, N., Couzis, A. and Maldarelli, C. (2003) *Journal of Colloid and Interface Science,* **267,** 272-285.

Kumar, N., Maldarelli, C. and Couzis, A. (2006) *Colloids and Surfaces A: Physicochemical and Engineering Aspects,* **277,** 98-106.

Lee, K. S. and Starov, V. M. (2007) *Journal of Colloid and Interface Science,* **314,** 631-642.

Lee, K. S. and Starov, V. M. (2009) *Journal of Colloid and Interface Science,* **329,** 361-365.

Lin, S. H., Ziv, A. R. and Eyring, H. (1981) *Proc. Natl. Acad. Sci. USA,* **78,** 3989-3992.

Myers, D. (2006) *Surfactant science and technology,* Wiley-Interscience, John Wiley & Sons, Inc., Hoboken, New Jersey.

Nagarajan, R. (2002) *Langmuir,* **18,** 31-38.

Nikolov, A. D., Wasan, D. T., Chengara, A., Koczo, K., Policello, G. A. and Kolossvary, I. (2002) *Advances in Colloid and Interface Science,* **96,** 325-338.

Njobuenwu, D. O. (2007) *Leonardo Journal of Sciences,* **6,** 153-164.

Rafai, S. and Bonn, D. (2005) *Physica A: Statistical Mechanics and its Applications,* **358,** 58-67.

Rafai, S., Sarker, D., Bergeron, V., Meunier, J. and Bonn, D. (2002) *Langmuir,* **18,** 10486-10488.

Ruckenstein, E. (1996) *Journal of Colloid and Interface Science,* **179,** 136-142.

Scales, P. J., Grieser, F., Furlong, D. N. and Healy, T. W. (1986) *Colloids and Surfaces,* **21,** 55-68.

Starov, V. M., Kosvintsev, S. R. and Velarde, M. G. (2000) *Journal of Colloid and Interface Science,* **227,** 185-190.

Stoebe, T., Lin, Z., Hill, R. M., Ward, M. D. and Davis, H. T. (1996) *Langmuir,* **12,** 337-344.

Stoebe, T., Lin, Z., Hill, R. M., Ward, M. D. and Davis, H. T. (1997) *Langmuir,* **13,** 7282-7286.

Svitova, T., Hill, R. M. and Radke, C. J. (2001) *Colloids and Surfaces A: Physicochemical and Engineering Aspects,* **183-185,** 607-620.

Svitova, T., Hill, R. M., Smirnova, Y., Stuermer, A. and Yakubov, G. (1998) *Langmuir,* **14,** 5023-5031.

Svitova, T., Hoffmann, H. and Hill, R. M. (1996) *Langmuir,* **12,** 1712-1721.

Tang, X., Dong, J. and Li, X. (2008) *Journal of Colloid and Interface Science,* **325,** 223-227.

Tanner, L. H. (1979) *J. Phys. D: Appl. Phys.,* **12,** 1473-1484.

Voinov, O. V. (1976) *Izv. Akad. Nauk SSSR, Mekh. Zhidk. i Gaza,* **76**.

von Bahr, M., Tiberg, F. and Yaminsky, V. (2001) *Colloids and Surfaces A: Physicochemical and Engineering Aspects,* **193,** 85-96.

von Bahr, M., Tiberg, F. and Zhmud, B. V. (1999) *Langmuir,* **15,** 7069-7075.
Zhang, Y., Zhang, G. and Han, F. (2006) *Colloids and Surfaces A: Physicochemical and Engineering Aspects,* **276,** 100-106.
Zhu, S., Miller, W. G., Scriven, L. E. and Davis, H. T. (1994) *Colloids and Surfaces A: Physicochemical and Engineering Aspects,* **90,** 63-78.
Zolotarev, P. P., Starov, V. M. and Churaev, N. V. (1976) *Colloid. J.(USSR Academy of Sciences, English Translation,* **38,** 895.

Chapter 3 : Materials and Methods

3.1 Experimental Techniques

Numerous methods and techniques have been developed for experimental investigation of wetting and spreading properties of liquid-solid systems. In this thesis performance of surfactant solutions was assessed using classical drop-measurement methods. For contact angle, radius, height and volume of the drop, the sessile drop technique was used, while for measuring surface tension of various solutions the pendant drop method was employed. All experiments were filmed using either CCD (Flee 2, Point Grey Research, Canada) or high-speed (Motion BLITZ HSC, Mikrotron GmbH, Germany) cameras operating at different frame rates. Recorded sequences were subsequently analyzed using drop shape analysis software from *First Ten Angstroms*®, Portsmouth, VA. A powerful white LED backlight with a diffuser was used as a light source, in order to minimize heating of the drop, yet allowing uniform lighting and good contrast (Figure 3.1). Prior to each experiment calibration of FTA software was carried out, either by a liquid with known surface tension e.g. distilled water with γ = 72 mN/m at room temperature ~ 25° C, or by known outer diameter of the needle used. Syringes, needles and substrates used were rinsed with acetone and afterwards thoroughly washed with water purified by the Barnstead NANOpure Diamond water system and dried at room temperature before each measurement. In order to substantiate that the properties of the substrates remained unchanged after cleaning, static contact angles of pure water were measured on each substrate prior to each experiment, verifying that our cleaning routine was satisfactory for the particular types of surfactants and substrates used in this thesis. Each experiment was repeated at least five times; the differences between measured values were insignificant, within the margins of the experimental error of the techniques used, proving high reproducibility of our measurements.

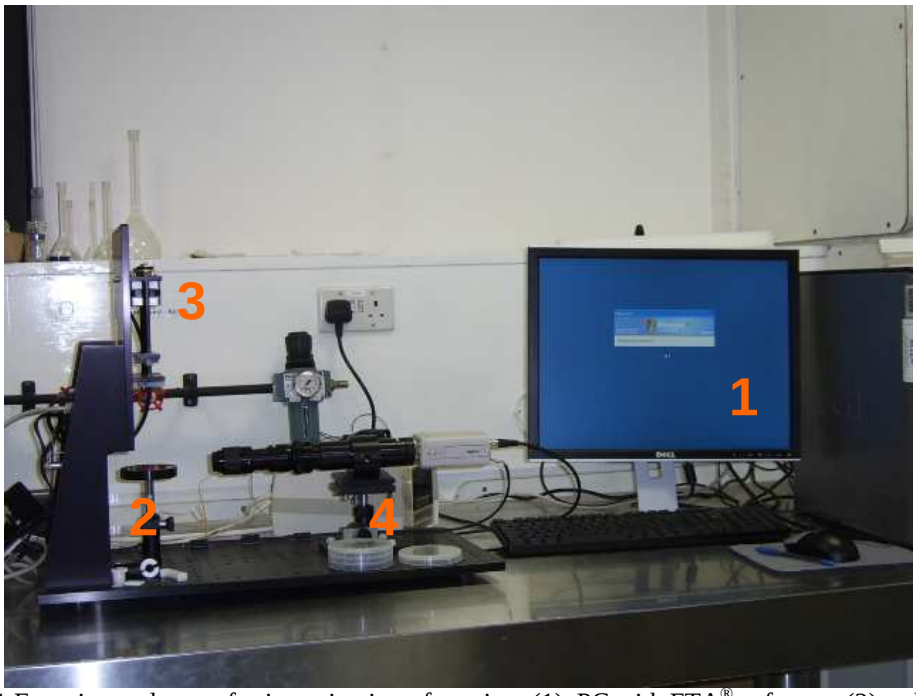


Figure 3.1 Experimental setup for investigation of wetting; (1), PC with FTA® software; (2), substrate holder; (3), microsyringe with blunt needle for precise drop deposition; (4), CCD/High-speed camera with magnifying lens

3.1.1 Pendant Drop Method

Pendant drop technique is a reliable tool for measuring surface and/or interfacial tension of the liquid. Since the early works of Bashforth and Adams (Bashforth and Adams, 1883) and Andreas et al. (Andreas et al., 1938) it is considered to be a classical and often used method for quantifying interfacial tension of various liquids (Song and Springer, 1996a, Song and Springer, 1996b, del Río and Neumann, 1997). In our experiments, controlled volume of tested liquid was pushed through the micro-needle with blunt tip, either manually or automatically (using a programmable syringe pump), and formed hanging drop was let to reach its hydrodynamical and mechanical equilibrium. Typical drop shape at the equilibrium is governed only by gravitational forces and interfacial tension and from the geometrical profile of the pendant drop the interfacial tension can be calculated using equations from the literature (Anastasiadis et al., 1987). In this thesis only surface (*l-g*) tension of

surfactant solutions were measured and the calculations were automatically done by the FTA software. Values of the surface tension are determined according to the Equation 3.1 (Adamson and Gast, 1997):

$$\gamma_{lg} = \frac{\Delta\rho g d_e^2}{H} \tag{3.1}$$

where $\Delta\rho$ is difference in density between the drop and the surrounding environment, g is acceleration of gravity, d_e is the equatorial diameter of the drop and H is a shape-dependent quantity. $1/H$ acts as correction factor that is defined by d_s/d_e ratio, where d_s is the diameter measured at a distance d_e from the bottom of the drop, as shown in Figure 3.2 (a). Calibration measurements were carried out with pure distilled water with known surface tension of 72 mN/m (Figure 3.2 (b))

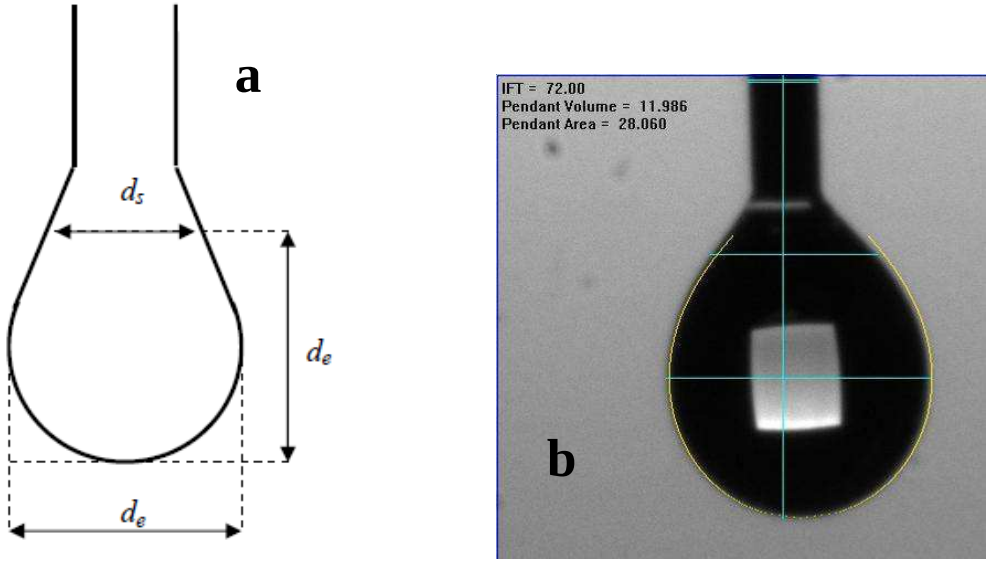


Figure 3.2 Pendant drop method for measuring surface tension of a liquid

3.1.2 Sessile Drop Method

Rapid development of digital image processing in the second half of the previous century and the use of computers allowed various geometrical parameters to be easily extracted from a drop image and calculated in the similar manner as surface tension above. Using the profile of a sessile drop to determine the contact angle between the liquid drop and the solid surface introduced a novel approach in interfacial phenomenon investigation (De Coninck, 1994 and references within). Nowadays drop shape analysis is a convenient way to measure not only the contact angle, but also the other geometrical parameters of the sitting drop: radius, height and volume (Figure 3.3 (a)). Additional advantages of the method are that it is irrelevant from which direction the drop is viewed (the drop is assumed symmetric about a central vertical axis) and that it can be used for dynamic measurements. FTA software allows the measurement of the dynamic contact angle with an estimated experimental error of ± 1° and ± 0.1 mm for drop radius and height.

Main weaknesses of the method arise from the assumed sphericity of the drop. For sufficiently small liquid drops the influence of gravity becomes negligible and the fluid forms a spherical shape (Picknett and Bexon, 1977, Leger and Joanny, 1992). If drop forms a spherical cap its volume and area may be calculated using any two geometrical parameters: r, h or θ (Figure 3.3 (b)). However, when sessile drops are flattened they lose their sphericity. This issue has been mentioned in literature and several models have been suggested (Meric and Erbil, 1998, Erbil and Meric, 1997). These include three-parameter spherical cap, ellipsoidal cap and pseudo-spherical cap models. However, to the best of my knowledge, these have not been implemented into commercial software yet. FTA allows users to choose between spherical and non-spherical fit and these were used appropriately: spherical fit at sufficiently high contact angles and non-spherical fit for smaller ones.

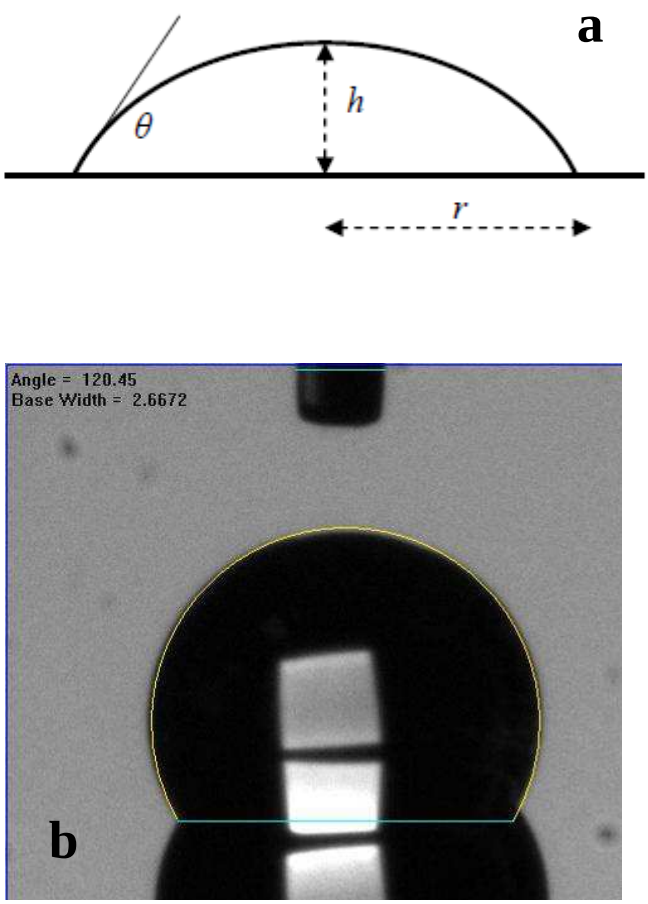


Figure 3.3. Sessile drop - geometrical parameters

3.1.3 Capillary Rise

Spontaneous rise of liquids in thin capillaries is an intriguing phenomenon that is often employed as experimental technique due to its simplicity: surface tension pulls the liquid up the tube until gravitational forces are sufficient to overcome the intermolecular forces. The freshly prepared surfactant solution was placed in a cylindrical glass dish filled up to the rim. The glass capillary was positioned above the glass dish normal to the surface of the solution and the capillary was then brought in contact with the solution (Figure 3.4). The rise of the liquid was recorded and

captured sequences were subsequently analyzed using Image-Pro® analysis software by monitoring the progress of the liquid front as a function of time (Figure 3.5).

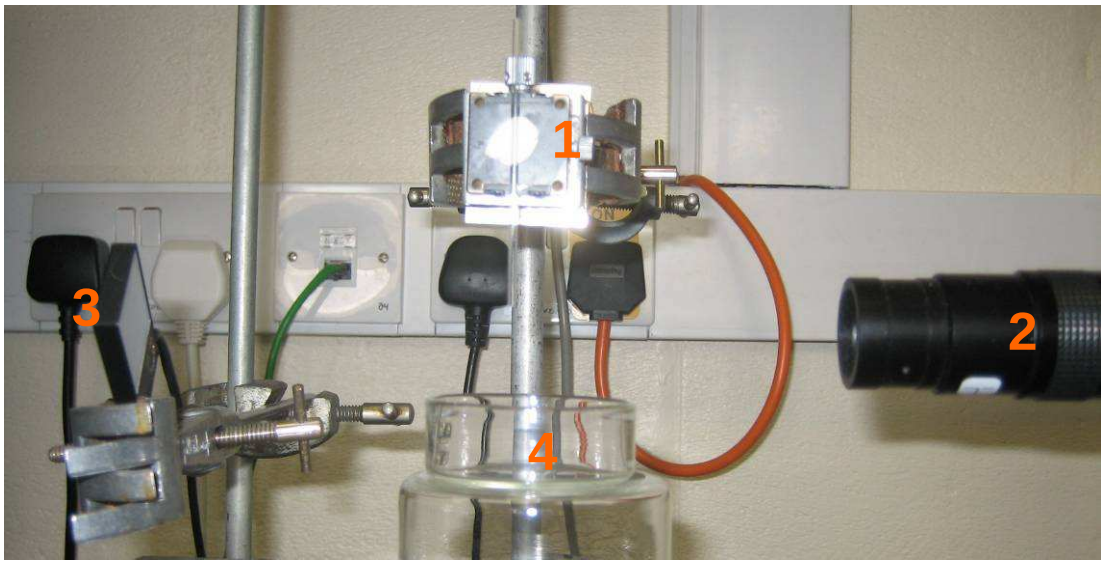


Figure 3.4 Experimental setup for investigation of the capillary rise; (1), glass capillary; (2), High-speed camera with magnifying lens; (3), LED backlight; (4), dish with trisiloxane solution

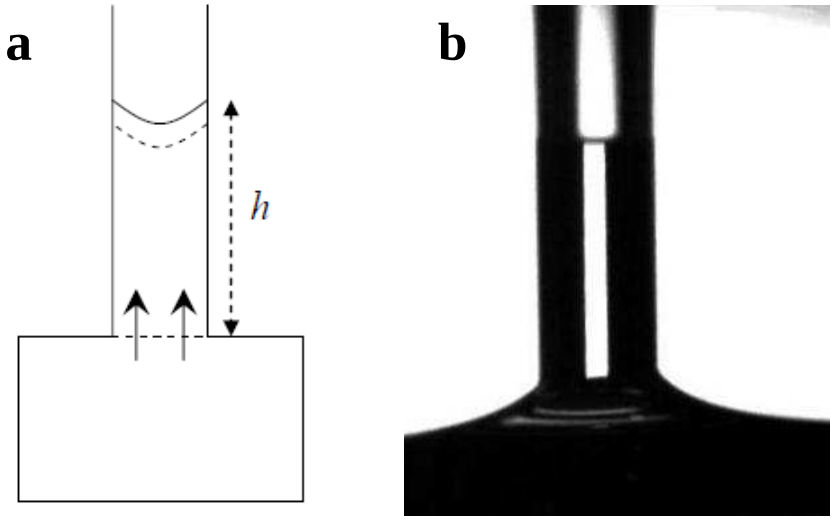


Figure 3.5 Spontaneous liquid rise in glass capillaries

3.2 Materials

3.2.1 Surfactants

In this thesis two types of trisiloxane superspreaders were tested. The superspreaders (polyalkyleneoxide modified heptamethyltrisiloxane) used were Silwet L-77® and Additive 67®. Silwet L-77® (De Sangosse Ltd, Cambridge, UK) is a commercial trisiloxane surfactant with concentration between 80 – 85 %, while Additive 67® (Dow Corning Co., Coventry, UK) contains 76 % of trisiloxane component. Performance of superspreaders was compared to that of a conventional nonionic surfactant, Triton X-100® (octylphenol ethylene oxide condensate), a pure surfactant obtained from Sigma, Missouri, USA. Surfactant solutions were prepared with water, purified by the Barnstead NANOpure Diamond water system. All surfactants were used as received without further purification.

3.2.2 Substrates

Substrates used were smooth silicon wafers coated with different polymer films. While the coating changes the substrate surface energy, it does not alter the roughness of the surface, and AFM surface scanning proved polymer coating to be essentially ideally smooth, with roughness in the range of nanometres (Figure 3.6). Polymer films were deposited using spin coating technique, which allows controlling the thickness and the roughness, with subsequent curing. Deposited coatings included polyxylylene polymer, Parylene® and fluorocarbon polymers, Cytop® and Teflon®, which exhibit, respectively, increasing degrees of hydrophobicity. Equilibrium contact angles of pure water drops on these surfaces are 89°, 110° and 120°, respectively. Prior to each experiment, substrates were rinsed with acetone and afterwards thoroughly washed with purified water and dried at room temperature.

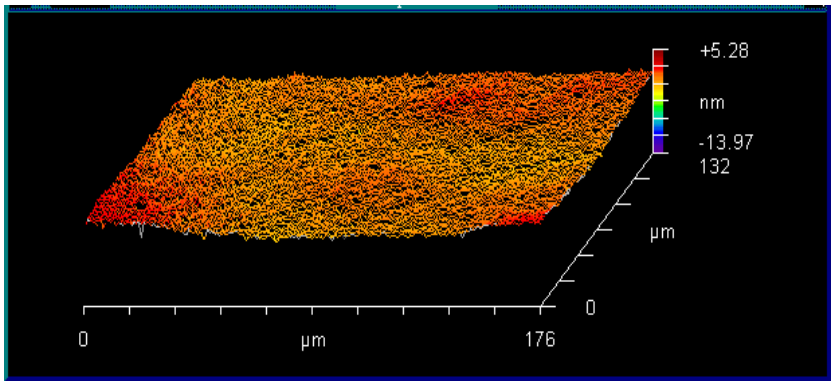


Figure 3.6 Surface roughness profile obtained with a microscope interferometer (New View 100, Zypo Corp, USA).

3.2.3 Capillary tubes

The capillaries used in experiments were borosilicate glass capillaries with 1.63 mm diameter, purchased from Drummond Scientific Company. Prior to each experiment, capillaries were cleaned with acid and alkaline solutions, rinsed with purified water and afterwards dried in stream of clean air.

3.3 References

Adamson, A. W. and Gast, A. P. (1997) *Physical Chemistry of Surfaces,* John Wiley and Sons, Inc, New York.

Anastasiadis, S. H., Chen, J. K., Koberstein, J. T., Siegel, A. F., Sohn, J. E. and Emerson, J. A. (1987) *Journal of Colloid and Interface Science,* **119,** 55-66.

Andreas, J. M., Hauser, E. A. and Tucker, W. B. (1938) *The Journal of Physical Chemistry,* **42,** 1001-1019.

Bashforth, F. and Adams, J. C. (1883) *An Attempt to Test the Theories of Capillary Action,* Cambridge Univ. Press, Cambridge.

De Coninck, J. (1994) *Colloids and Surfaces A: Physicochemical and Engineering Aspects,* **89,** 109-115.

del Río, O. I. and Neumann, A. W. (1997) *Journal of Colloid and Interface Science,* **196,** 136-147.

Erbil, H. Y. and Meric, R. A. (1997) *The Journal of Physical Chemistry B,* **101,** 6867-6873.

Leger, L. and Joanny, J. F. (1992) *Reports on Progress in Physics,* **55,** 431.

Meric, R. A. and Erbil, H. Y. (1998) *Langmuir,* **14,** 1915-1920.

Picknett, R. G. and Bexon, R. (1977) *Journal of Colloid and Interface Science,* **61,** 336-350.

Song, B. and Springer, J. (1996a) *Journal of Colloid and Interface Science,* **184,** 64-76.

Song, B. and Springer, J. (1996b) *Journal of Colloid and Interface Science,* **184,** 77-91.

Chapter 4 : Trisiloxanes on Hydrophobic Surfaces

Since the early 90's, silicone surfactants and particularly trisiloxanes have been subject to an increasing interest because of their exceptional spreading properties. The superiority of trisiloxanes over common surfactants has been clearly demonstrated in the last decade. However, a full understanding of the exceptional enhanced spreading of trisiloxanes is still lacking. Previous studies were mainly performed on hydrophilic substrates where superspreaders have proved to be matchless. However, their behaviour on hydrophobic substrates has not been thoroughly investigated.

4.1 Trisiloxanes vs Conventional Surfactants

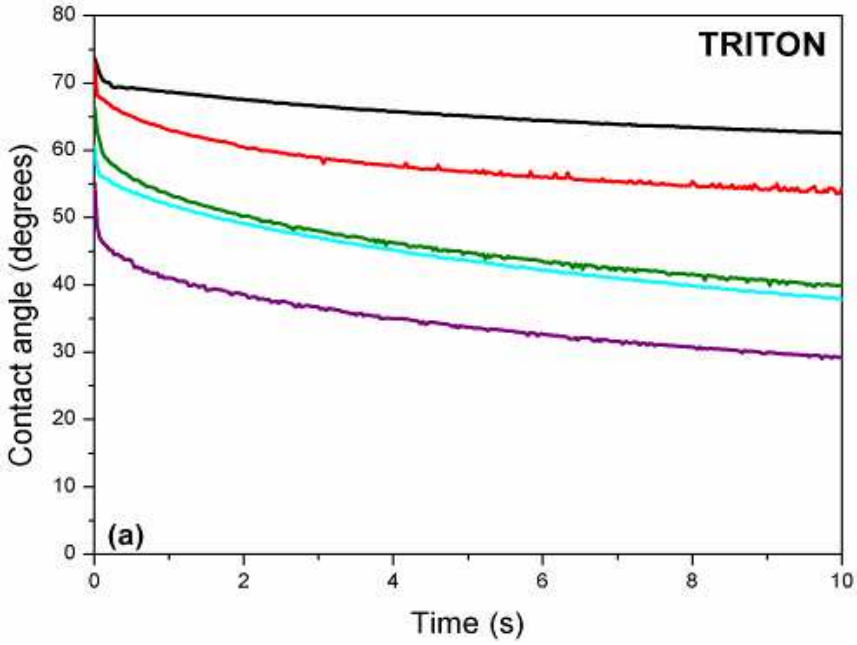
Wetting of water-based Silwet® L-77 solutions was investigated on ideally (defect-free) smooth polymer surfaces. Equilibrium contact angles of water drops on Parylene®, Cytop® and Teflon® were 89°, 110° and 120°, respectively (Table 4.1). Wetting on Parylene® was especially interesting to study, as it lies at "wetting limit" between hydrophilicity and hydrophobicity, with a water contact angle of 88°-90°. For comparison we chose conventional Triton® X-100 surfactant as a reference. Five solutions of varying surfactant concentration were tested: 0.00625, 0.0125, 0.025, 0.0625 and 0.125 wt %, which in fact correspond to 0.5, 1, 2, 5 and 10 CMC for Triton® X-100 solutions. Drops of few microliters in volume were deposited from very small height (few mm); hence gravitational effects were considered to be negligible. Measured equilibrium contact angle values for both surfactant solutions are presented in Figure 4.1.

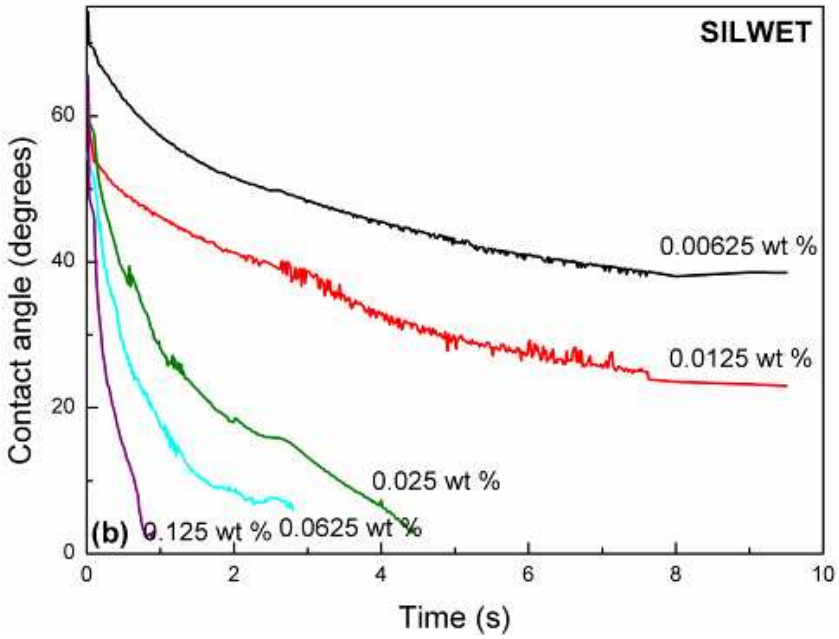
Table 4.1. Final contact angle values of water and 0.025 wt % surfactant water-based solutions on various surfaces.

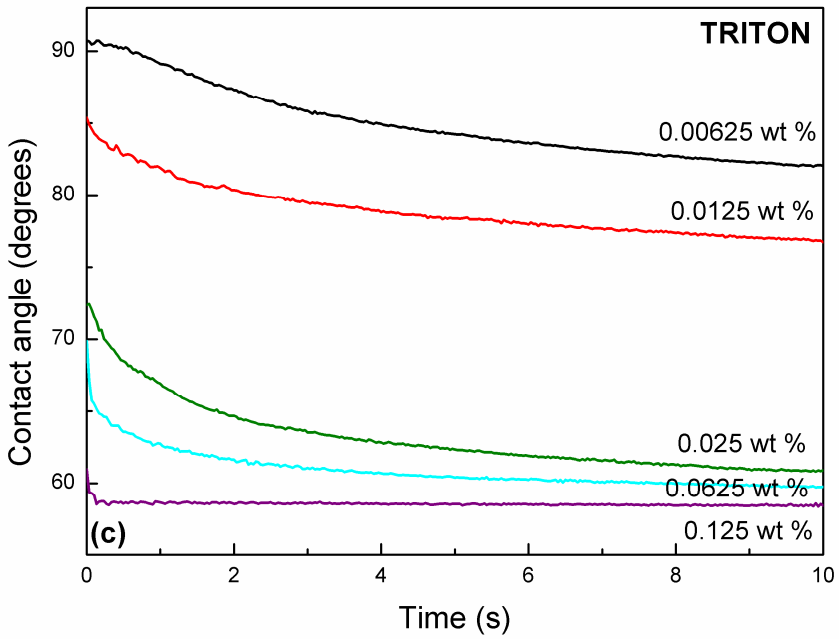
	Water	*Triton® X-100*	*Silwet® L-77*
Parylene	*88-90°*	*40°*	*~0°*
Cytop	*110°*	*60°*	*30°*
Teflon	*120°*	*77°*	*51°*

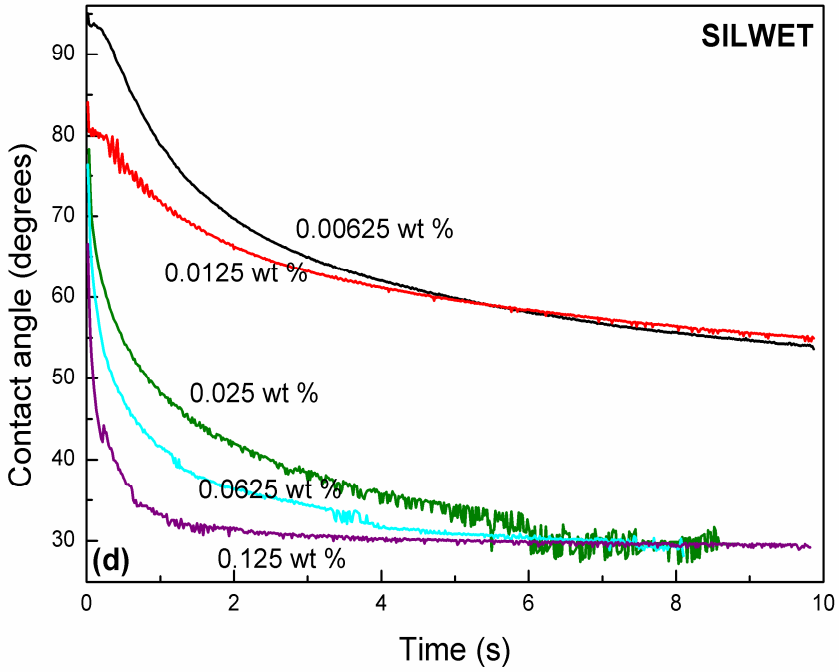
4.1.1 Triton® X-100

As shown in Figure 4.1 (a), (c), (e), the addition of Triton® X-100 to water resulted in faster and improved wetting, giving lower contact angles on all substrates. From Figure 4.2 it can be seen that Triton® X-100 solutions showed a decreasing final contact angle with the increasing concentration. The significant reduction in contact angle was found to be approximately constant for solutions above 2 CMC, although a very slight decrease was observed. This limiting reduction in contact angle may be expected to occur at ~1 CMC, but our results suggest about twice this value. However, this is not surprising since at 1 CMC the surfactant solution is not effectively saturated, as far as surface effects are considered, since micelles act as surfactant "reservoirs". This general trend was observed on all surfaces, with the higher the final contact angle for the more hydrophobic surface. The asymptoting of the values of contact angle for high surfactant concentrations is general, although some evolution still seems to occur. This is perhaps related to the spreading kinetics (the flow-controlled availability of surfactant molecules) and possibly to a degree of wetting hysteresis hindering final attainment of thermodynamic equilibrium. In the case of Parylene®, even for the highest concentration (10 CMC) of Triton® X-100, the final (steady) contact angle could not be measured within 10 seconds.


TRITON
Contact angle (degrees)
Time (s)
(a)
0
10
20
30
40
50
60
70
80
0
2
4
6
8
10


SILWET
Contact angle (degrees)
Time (s)
(b)
0.00625 wt %
0.0125 wt %
0.025 wt %
0.0625 wt %
0.125 wt %
0
20
40
60
0
2
4
6
8
10


TRITON
0.00625 wt %
0.0125 wt %
0.025 wt %
0.0625 wt %
0.125 wt %
(c)
Contact angle (degrees)
Time (s)
90
80
70
60
0
2
4
6
8
10


SILWET
0.00625 wt %
0.0125 wt %
0.025 wt %
0.0625 wt %
0.125 wt %
(d)
Contact angle (degrees)
Time (s)
90
80
70
60
50
40
30
0
2
4
6
8
10

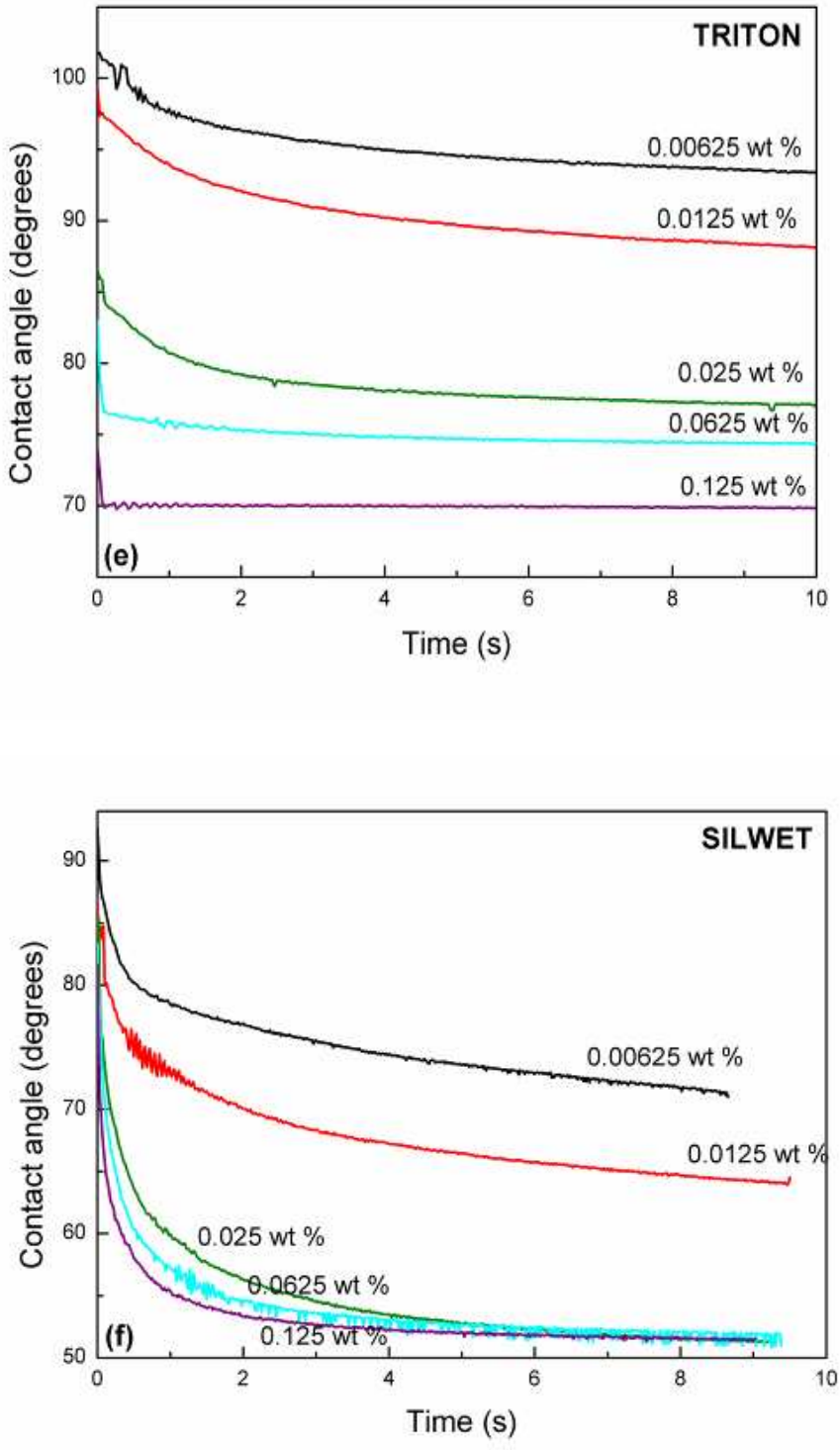


Figure 4.1 Contact angle vs. time for aqueous Triton® X-100 and Silwet® L-77 solutions on (a, b) Parylene, (c, d) Cytop and (e, f) Teflon.

4.1.2 Silwet® L-77

By comparing Figures 4.1 (b), (d), (f) with Figures 4.1 (a), (c), (e), at equal surfactant concentrations the kinetics of spreading on all surfaces is considerably faster in the case of Silwet® L-77. In addition, the final contact angles for Silwet® L-77 solutions were found to be significantly lower than those of equivalent Triton® X-100 solutions. The most obvious wetting improvement was noticed on the least hydrophobic substrate, Parylene, on which Silwet® L-77 exhibited (total) spreading for high concentrations (0.025 wt % and above). Drops of 0.025 wt % Silwet® L-77 solution spread completely on the Parylene surface within ~ 4 seconds, and for higher concentrations, thin liquid films with no measurable contact angle were formed very quickly (in less than 3 seconds). On hydrophobic substrates, Cytop® and Teflon®, improved wetting was observed. For lower concentrations, the final contact angle value decreased with increasing surfactant concentration, while for higher concentrations (0.025 wt % and above) the same final contact angle value was reached. However, the observed spreading kinetics was different; spreading rate increased with surfactant concentration thus decreasing the time required to reach the final contact angle. Although CMC for Silwet® L-77 is not available, it is interesting to note that 0.025 wt % corresponds to 2 CMC in the case of Triton® X-100. Thus, as clearly shown in Figure 4.1, on all substrates, the optimal concentration of *either* surfactant was found to be 0.025 wt % (corresponding to 2 CMC for Triton® X-100). Furthermore, trends observed in Figure 4.1 may potentially be used as an alternative way to estimate CMC/CWC of Silwet® L-77 surfactant.

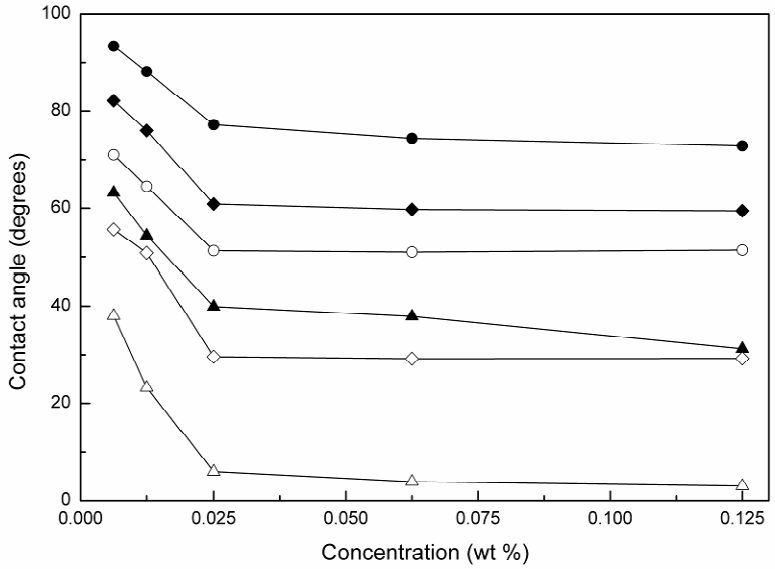


Figure 4.2 Final contact angle values of Triton® X-100 (solid symbols) and Silwet® L-77 (open symbols) water-based solutions. Δ, Parylene; ◊, Cytop; and ○, Teflon.

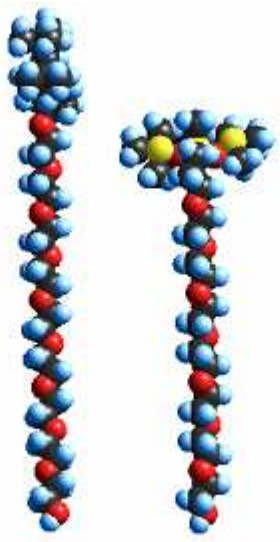


Figure 4.3 Molecular structures of the alkyl polyethoxylates and trisiloxane surfactants. Red atoms are oxygen; black atoms are carbon; blue atoms are hydrogen; and yellow atoms are silicon.

For both conventional Triton® X-100 and the superspreader Silwet® L-77, the final contact angle monotonically decreased with increasing concentration until a certain value is reached above which further increase in surfactant concentration did not improve wetting any further. We have ascertained that this limiting (saturation) concentration was 0.025 wt % for both surfactants. However, Silwet® L-77 solutions exhibited a final contact angle 30° lower than Triton® X-100 solutions in the case of Parylene® and Cytop®, and 20° on Teflon®. The superiority of Silwet® L-77 is may be related to the specific 'T' shape of the trisiloxane molecule. As shown in Figure 4.3, the cross-sectional area of the hydrophilic tail of the Triton® X-100 molecule is very similar to that of Silwet® L-77, and the main difference between the two surfactant molecules is that the hydrophobic head of Silwet® L-77 is significantly different in shape and size than that of Triton® X-100, thus (presumably) allowing more effective adsorption at the interface, hence leading to a more efficient decrease in surface tension. This has been confirmed by surface tension measurements, using the pendant drop method (Figure 4.4). For Triton® X-100 solutions, an increase in concentration resulted in lower values of surface tension, although higher Triton® X-100 concentrations exhibited similar values at ~ 30 mN/m. For lower concentrations of Silwet® L-77 solutions, a linear decrease in surface tension was noted, while for all higher concentrations, surface tension value was constant at ~ 23 mN/m. The Silwet® L-77 solutions are quite clearly liquids of lower surface tension than solutions of Triton® X-100, at equal concentration. A suggested explanation is that, from a critical concentration onwards, most of the surfactant molecules that can possibly occupy the free surface of the solution have already migrated there. However, in the case of Silwet® L-77, trisiloxane molecules are more *efficiently* adsorbed on the liquid/gas interface than in the case of Triton® X-100, leading to less exposed water and therefore a lower surface free energy, or surface tension.

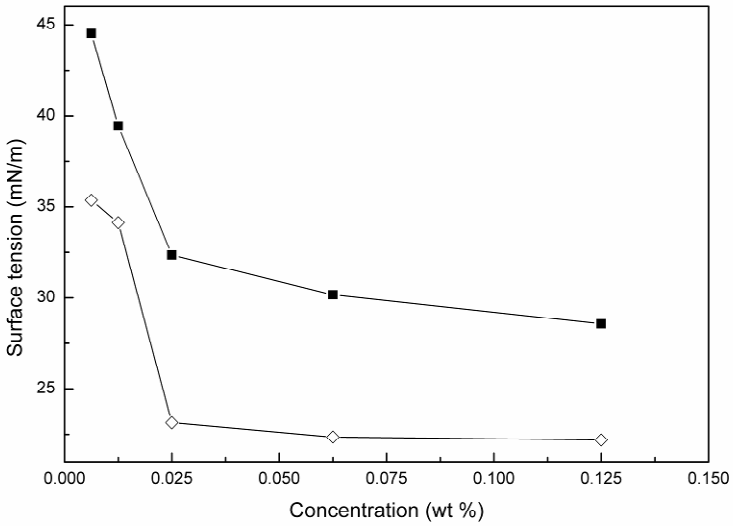


Figure 4.4 Final (steady) surface tension values of water-based solutions of Triton® X-100 (solid symbols) and Silwet® L-77 (open symbols) as a function of concentration.

Lower values of surface tension and lower contact angles on a given substrate represent equivalent behaviour. The critical concentration, at which the solution fairly abruptly changes its behaviour, was found to be 0.025 wt % for both surfactants and a further increase in concentration did not greatly affect surface tension or wetting ability. Final contact angle values for 0.025 wt % solutions, which we consider optimal, are presented in Table 4.1. As noted above, for concentrations above this, no further decrease in final contact angle was observed for Silwet® L-77 and only a slight decrease for Triton® X-100. Based on the theory of micelles, we propose the following scheme. During the initial wetting phase, solubilised surfactant molecules (probably) immediately adsorb at the interface, leading to lower initial values of contact angle. Diffusion from the micelles into the solution takes place, as more surfactants are needed to “replace” solubilised surfactant molecules, which had already adsorbed at the ‘initial’ interface. Improved wetting behaviour is apparent as further surfactant adsorption occurs at the expanding interface. Once the limiting final value has been reached, no more surfactant molecules can be adsorbed at the interface and the diffusion process stops. Any further increase in concentration cannot lead to additional wetting improvement. This limiting contact angle value

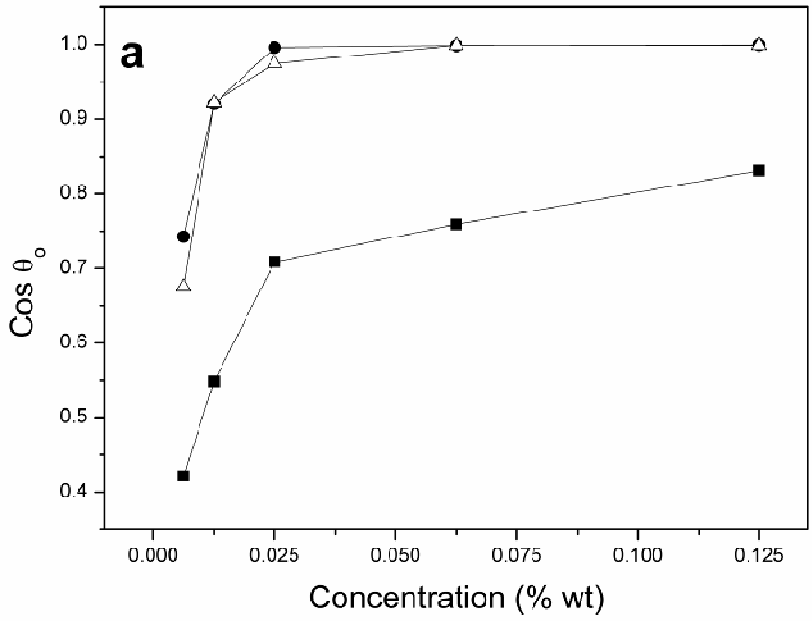
depends on the type of surfactant and its concentration, but more significantly on the nature of the substrate. For the case of very smooth surface without defects, hydrophobicity was proven to be the main limiting factor. The above fits in well with micelle theory, a main conclusion being that the Silwet® L-77 presents generally lower contact angles and lower surface tension, probably related to better surface coverage.

4.1.3 Additive® 67

Both Silwet L-77® and Additive 67® are commercial trisiloxane products widely used in numerous practical applications nowadays. However, it should be noted that since these products have different quantities of the trisiloxane active ingredient, it could be expected to show different spreading performance. Additionally, Silwet L-77® is a yellow liquid with a boiling point of 160° C, while Additive 67® is an amber-coloured liquid which boils at 100° C. This information suggests that significant differences, other than simply trisiloxane content, exist between the two liquids to cause such a vast difference in boiling points. A maximum of 10 % difference by weight of trisiloxane molecules is unlikely to be the explanation of colour variation. We suspect that the nature and the quantity of additives in commercial surfactant products may be the main reason. Furthermore, these may significantly contribute to the overall spreading behaviour.

The results of wetting of "pure" solutions of both superspreaders, Silwet L-77® and Additive 67®, are presented in Figure 4.5 as cosine of the equilibrium contact angle, cos θ_o, depending on the concentration of surfactant, for three aforementioned solid surfaces. In all cases, increasing surfactant concentration led to significant reductions in contact angle. The evolution of $cos\ \theta_o$ with concentration, in Figure 4.5 reflects the degree of hydrophobicity of the substrate. For a given concentration of a given surfactant, $cos\ \theta_o$ is highest for the Parylene®, followed by Cytop® and then finally Teflon® gives the largest angles. Data for maximum and minimum angle values observed, as well as those of pure water for comparison, are given in Table 4.2. Clearly, the hydrophobic tendency is there, whether or not a superspreader is present in the liquid drop.

The evolution of these curves is of interest. No information on average molecular weight or chain length distribution was available for these products, and since they are mixtures of trisiloxane molecules with additives, CMC values cannot be readily determined. However, simple drop wetting experiments revealed the concentrations above which (equilibrium) wetting did not improve (the lowest value of θ_o for a given solid). Below these critical concentrations, spreading ability was found to improve with increasing surfactant concentration (see Figure 4.5). The results revealed that aqueous solutions of both trisiloxane-based surfactants reached similar final equilibrium contact angles, on a given polymeric surface, while conventional surfactant solution exhibited significantly higher angles. However, as indicated above, measured values were found to be largely dependent on solid surface hydrophobicity.



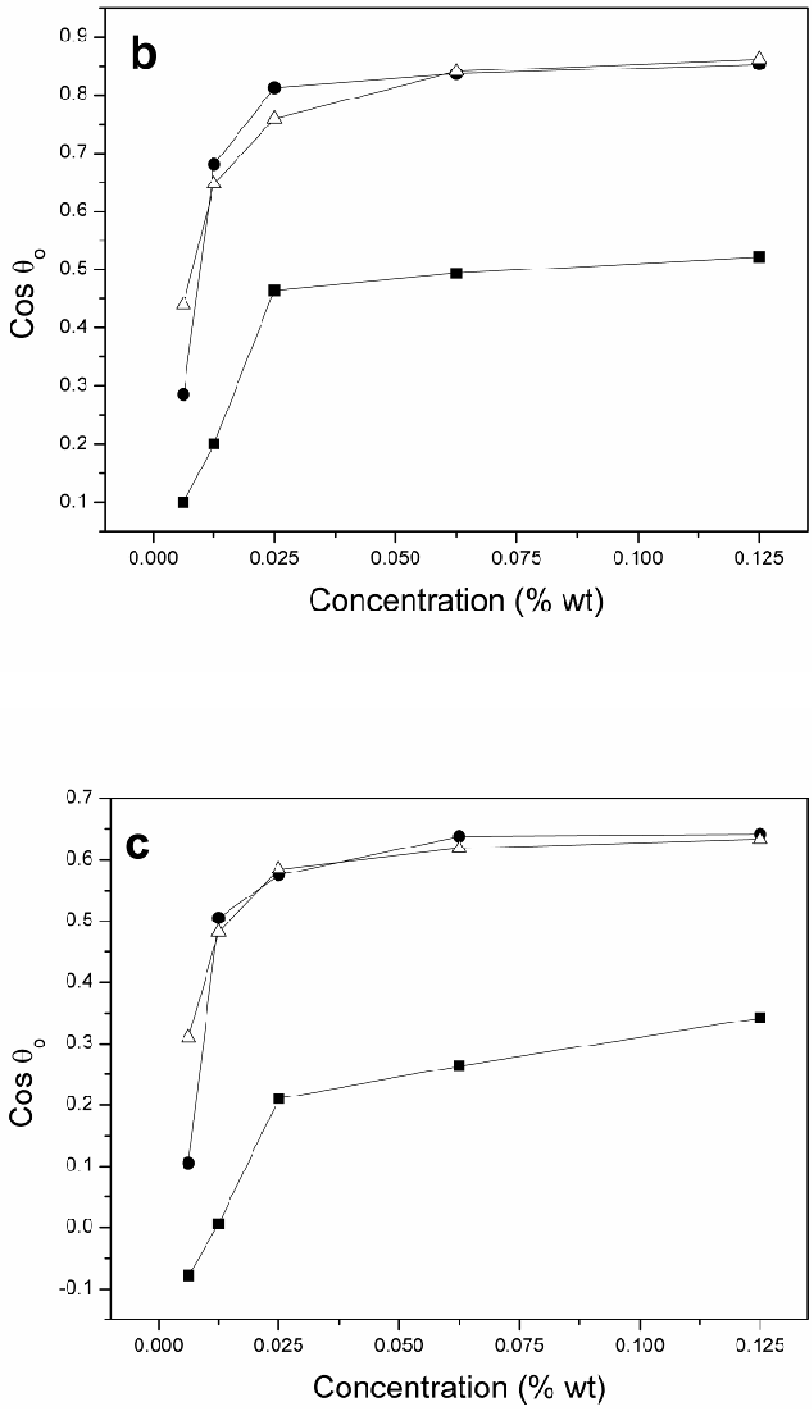


Figure 4.5 Cosine of equilibrium contact angles for different aqueous surfactant solution concentrations on (a) Parylene®, (b) Cytop®, and (c) Teflon®. Symbols used are: Δ, Additive 67®, ●, Silwet L-77®, and ■, Triton X-100®.

Table 4.2. Values of equilibrium contact angle, θ_o, of drops of water and "pure" superspreader surfactant solutions of the minimum and maximum concentrations studied on the three polymeric substrates.

	Liquid	*Water*	*Silwet L-77®/Water*		*Additive 67®/Water*	
	Conc. (wt %)	*0*	*0.00625*	*0.125*	*0.00625*	*0.125*
θ_o (°) on Solid	*Parylene®*	*89*	*42*	*~ 0*	*48*	*~ 0*
	Cytop®	*110*	*73*	*30*	*64*	*30*
	Teflon®	*120*	*84*	*50*	*72*	*50*

Different trends were noticed on the slightly hydrophilic Parylene, compared to those observed on relatively hydrophobic Cytop® and Teflon®. Silwet L-77® was found to be more effective than Additive 67® on Parylene (see Figure 4.5 (a)). Total spreading (to all intents and purposes: θ_o very near 0) was observed at a Silwet L-77® concentration of 0.025 wt %, while this concentration of Additive 67® was insufficient to cause total spreading on Parylene®. This can perhaps be associated to a difference in concentration of trisiloxane molecules in the original commercial superspreaders. Similar values of equilibrium contact angles were measured for the aqueous solutions of Additive 67® and Silwet L-77® on the two more hydrophobic substrates, for all concentrations above 0.025 wt %. We thus suspect this value to be close to the "critical" concentration, and therefore in the vicinity of the theoretical CMC value for trisiloxane surfactants (see Figure 4.5 (b) and (c)). The lowest concentration examined, 0.00625 wt %, gave some insight into trisiloxane induced spreading improvement at concentrations below the (assumed) CMC. On both hydrophobic surfaces, Additive 67® showed significantly lower contact angles than those of Silwet L-77®. This may possibly be related to additives present in the commercial surfactant, which improve spreading on hydrophobic substrates. On the other hand, on slightly hydrophilic Parylene®, this was not the case, as the least concentrated solution showed Silwet L-77® to wet (marginally) better than Additive

67® on hydrophilic surfaces. Unexpected decrease in contact angle values below CMC can be explained in terms of stronger adsorption of impurities on the interface compared to adsorption of trisiloxane molecules. However, this is only possible at surfactant concentrations below CMC, as above CMC impurities tend to be efficiently packed within micelles. At higher surfactant concentrations, trisiloxanes govern the spreading dynamics and the nature of impurities is irrelevant, as it does not affect the overall spreading performance.

4.2 Conclusions

The spreading abilities of solutions of conventional Triton® X-100 and superspreaders Silwet® L-77 and Additive 67® surfactants were investigated experimentally. For both Triton® X-100 and Silwet® L-77 water based solutions, 0.025 % wt. was found to be the concentration for optimal spreading. However, Silwet® L-77 showed superiority on all surfaces, thus attaining lower surface tensions than Triton® X-100 solutions of the same concentration. It was shown that Silwet® L-77 solutions can lead to total spreading even on marginally hydrophilic Parylene®, while on hydrophobic surfaces final contact angles were always measurable.

Silwet L-77® and Additive 67®, commercial superspreader products, were compared in order to gain further insight into trisiloxane enhanced spreading. Aqueous solutions of these surfactants showed a significant spreading improvement, and for all concentrations above the estimated value of CMC, the measured contact angle values were almost equal. The effect of product additives was only important at very low concentrations, when Additive 67® showed better performance on hydrophobic surfaces. Generally it may be concluded that wetting capabilities of the commercial superspreaders, Additive 67® and Silwet L-77®, do not greatly differ on a number of surfaces with varying hydrophobicity.

Chapter 5 : Effect of Acetic Acid (Acidity) on Trisiloxanes

Trisiloxanes are commonly used as surfactants in the horticulture industry. They are compatible with the majority of pesticides and therefore are broadly recommended for numerous applications. Acidifiers are often added to pesticide mixtures, as alkaline water can significantly reduce the effectiveness of certain pesticides, such as the widely used organophosphate, organochlorine and carbamate insecticides in particular, which undergo a chemical reaction in the presence of alkaline water. Whilst alkaline hydrolysis of the pesticides modifies their active ingredients, in an acidic environment hydrolysis of the pesticides is prevented. Thus the protonated form will penetrate more rapidly than the ionized molecule (McMullan, 1996). Therefore, low pH is considered advisable when using pesticides. In addition to this, certain pesticides are weak acids themselves. The influence of pH on pesticide efficiency is well known and has been thoroughly investigated (Sheng et al., 2005). On the other hand, the effect of environmental conditions, such as the acidity, on the spreading process is still an open question.

5.1 Surfactants in Acidic Environment

In order to investigate whether pH of the solution will affect the wetting ability of surfactants we have used low pH solvents instead of water. Acidic Triton® X-100 and Silwet® L-77 solutions were prepared using diluted acetic acid: 0.1 M and 1.0 M, with pH values of 2.88 and 2.38, respectively. Equilibrium contact angles of the acetic acid solutions on the before mentioned polymer-coated surfaces are presented in Table 5.1 in comparison to those of water. Measured final contact angles of drops containing acetic acid on hydrophobic surfaces were found to be slightly greater than those of water, presumably due to the repulsive interactions between the polar acid molecules, dissociated ions and the non-polar substrate. On the other hand, slightly lower contact angles were measured on Parylene®, as attractive forces act between the slightly hydrophilic substrate and polar solution.

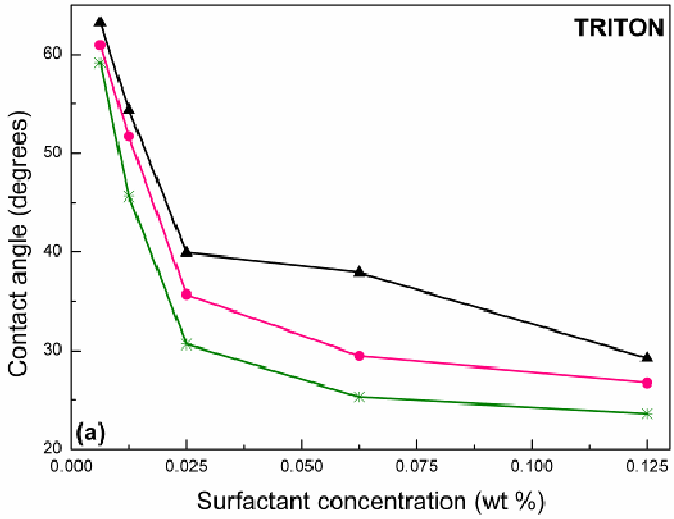
Table 5.1 Static contact angle values of water and 0.1 M and 1.0 M acetic acid solutions on various surfaces.

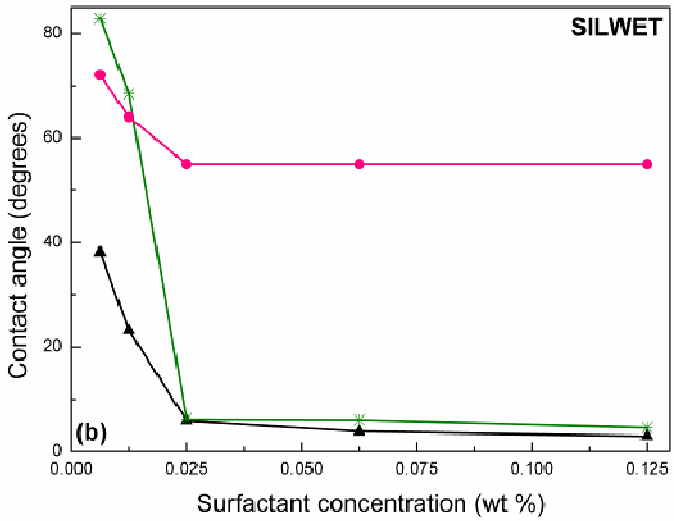
	water	*0.1 M acetic acid*	*1.0 M acetic acid*
Parylene	*88-90°*	*85°*	*76°*
Cytop	*110°*	*114°*	*116°*
Teflon	*120°*	*125°*	*128°*

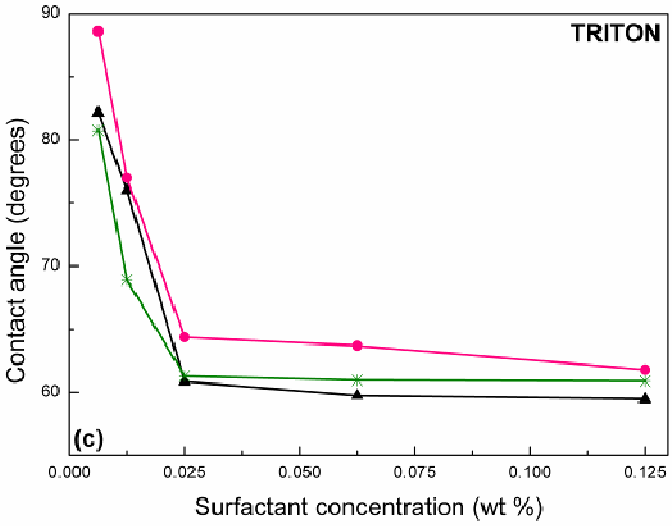
5.1.1 Triton® X-100

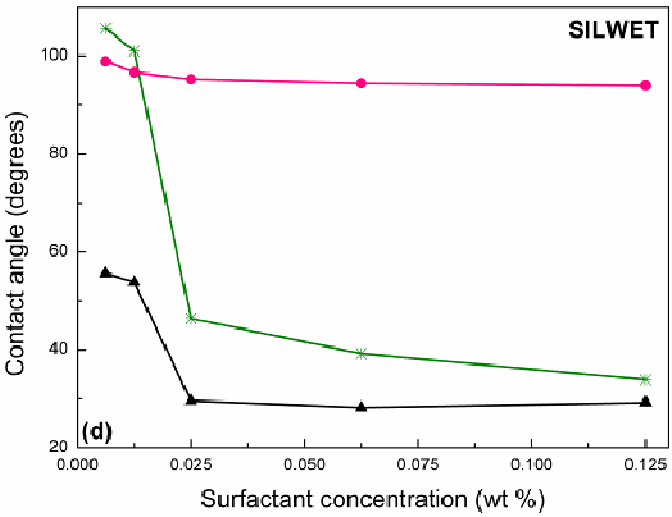
Acetic acid solutions containing Triton® X-100 surfactant reached lower contact angles on Parylene than water-based solutions. Intrinsically higher solid surface free energy is probably aided by the slight hydrophilicity of Parylene® (see Figure 5.1). However, the contact angle values of the 1.0 M acid solutions were higher than for the of 0.1 M acid solution. This was not the case for the hydrophobic substrates, Cytop® and Teflon®, where measured contact angles were higher than water-based ones, for ~ 5° for higher concentrations. In the case of Parylene®, the lower contact angles of low concentration 0.1 M acid solution drops is perhaps due to slower micelle formation, leading to an increased concentration of free surfactant molecules in the solution, more readily adsorbable at the liquid-solid interface, leading to better wetting. In the case of the hydrophobic polymers, due to repulsive forces between the substrate and acid ions in the solution, the contact angle value increased, as these repulsive interactions cannot be completely overcome at very low surfactant concentrations. At concentrations above CMC, there are enough surfactant molecules to adsorb at the interface and allow good wetting. No significant difference in final contact angle values was observed for either acid concentration, compared to water-based solutions. Neither micelle formation nor diffusion kinetics of Triton® X-100

solutions were significantly affected by the presence of acid molecules for concentrations above CMC, while below CMC acid concentration was found to be crucial. For 1.0 M acid solution with concentration below CMC, the concentration of acid ions in solution is higher, repulsive forces then govern the dynamics and affect the wetting process, ending in higher contact angle values.






TRITON
Contact angle (degrees)
90
80
70
60
(c)
0.000
0.025
0.050
0.075
0.100
0.125
Surfactant concentration (wt %)


SILWET
Contact angle (degrees)
100
80
60
40
20
(d)
0.000
0.025
0.050
0.075
0.100
0.125
Surfactant concentration (wt %)

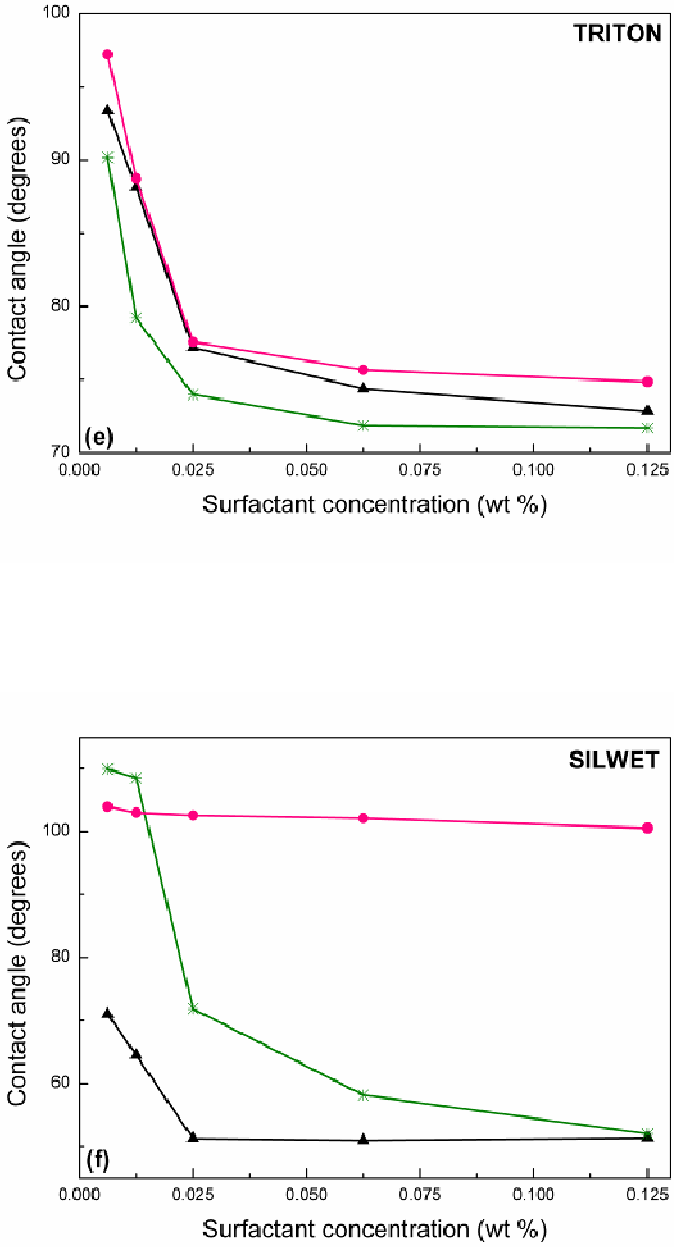


Figure 5.1 Final contact angle values for aqueous and acetic acid-based Triton® X-100 and Silwet® L-77 solutions on (a, b) Parylene, (c, d) Cytop and (e, f) Teflon. ▲, water (black); ∗, 0.1 M acetic acid solution (green); and ● 1.0 M acetic acid (pink).

5.1.2 Silwet® L-77

Unlike Triton® X-100, Silwet® L-77 superspreader surfactant was highly affected by the addition of acid (see Figure 5.1). On slightly hydrophilic Parylene® substrate, total spreading was observed for 0.1 M acid solution with surfactant concentrations above 0.025 wt %, while on hydrophobic surfaces, contact angles were surprisingly significantly higher compared to water solutions, although the difference decreased with increasing concentration. Solutions with the highest concentration of 0.125 wt % exhibited effective wetting with final contact angle value similar to that exhibited by water solutions. Poor wetting was noticed for 1.0 M acid solutions on all substrates: contact angles varied just a few degrees over five different concentrations, revealing a limiting contact angle value on each substrate, virtually independent of the surfactant concentration. Even on Parylene®, the contact angle was ~ 60°, whilst on the hydrophobic polymers the solutions could be considered as non-wetting (contact angle > 90°). The presence of acetic acid clearly reduced surfactant's activity. It was mentioned in (Wu and Rosen, 2002) that pH of the trisiloxane solution should be kept at 7, in order for surfactant to maintain its superspreading ability. At highly concentrated acid solutions, spreading was probably inhibited by polarization of the trisiloxane hydrophobic head (Snow et al., 1990). This would suggest that the polarized surfactant molecule was unable to adopt favourable conformations at the interface, thus leading to higher interfacial tension and consequently the higher contact angle. At low pH values, the mechanism of hydrolysis of the Si-O bond is thought to be the mechanism leading to loss of hydrophobicity of the molecular head and subsequently, the loss of its capacity to provoke superspreading. Due to ionisation of Si-O bond, solubility of the trisiloxane molecule is increased; it loses its interfacial ability, thus the increase in surface tension of the solution. Although polarization at high pH leads to some modification of the superspreader molecules, this was not evident for solutions of lower acid concentration. Polarization is probably not the main reason for poorer wetting of the less concentrated 0.1 M acid solutions. The inhibition of spreading possibly occurs because of the kinetic effect of hindered diffusion of surfactant molecules from the

bulk to the interface. Specific interactions between the (diluted) acid and trisiloxane molecules prevent surfactants from being adsorbed at the interface, as it is energetically more favourable to stay within the micelles. Nevertheless, this could be overcome by increasing surfactant concentration. Notwithstanding, for 0.1 M solutions below 0.025 wt % surfactant concentration, the presence of surfactants did not greatly affect the contact angle. This is presumably because almost no surfactant molecules were solubilised in the solution, but aggregated into micelles instead, showing contact angle values higher than 1.0 M solution. However, enhanced spreading was found at higher surfactant concentrations, confirming that trisiloxanes can maintain their good wetting ability at moderate pH if they are mixed into acid solution just prior to use (e.g. in pesticide spreading).

Surface tension measurements of the acetic acid surfactant solutions were performed using the pendant drop method (Figure 5.2). While Triton® X-100 solutions seemed unaffected by the addition of acetic acid, Silwet® L-77 solutions exhibited very different behaviour. The addition of acid to Triton® X-100 solutions did not affect surface tension values, the decrease in surface tension with the addition of surfactant being approximately the same with or without acid. For all three solvents, almost the same surface tension values were measured for all investigated concentrations. However, Silwet® L-77 acid-based solutions showed significant increases in surface tension compared to aqueous ones. The surface tension of 0.1 M acid surfactant solution showed a slight decrease compared to that of 0.1 M acetic acid solution without any surfactant added (Vazquez et al., 1997), while for 1.0 M acid solution surface tension measured low Silwet® L-77 concentrations was very similar to that of water and minor decrease was noticed only for highest surfactant concentration.

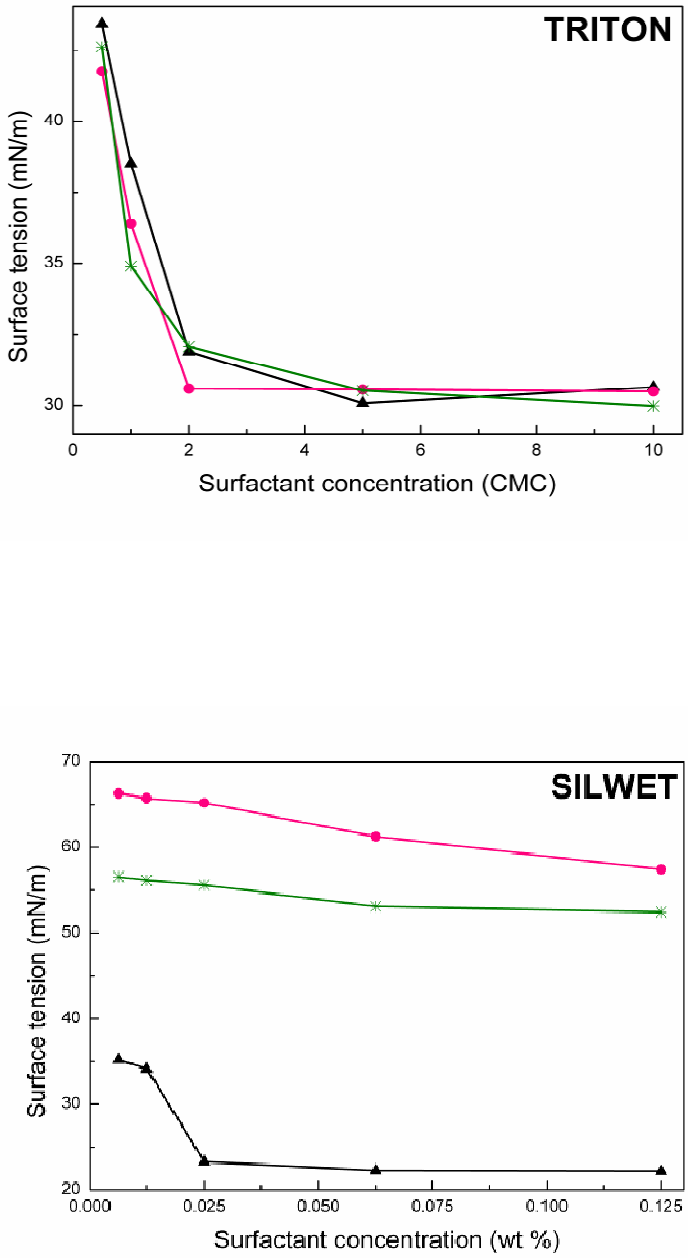


Figure 5.2 Final surface tension values for various aqueous and acetic acid-based solutions (a) Triton® X-100; (b) Silwet® L-77. ▲, water (black); ∗, 0.1 M acetic acid solution (green); and ● 1.0 M acetic acid (pink).

5.2 Conclusions

For Triton® X-100, 2 CMC (0.025 wt %) was found to be the optimal concentration for both water and acid-based solutions. Similar contact angle values were measured for all the 2 CMC Triton® X-100 solutions considered, for a given substrate, which shows that no major spreading obstruction is caused by the presence of the acid. However, Silwet® L-77 solutions showed different behaviour. For 1.0 M acetic acid solutions, the spreading was significantly hindered, while for 0.1 M acetic acid only the highest 0.125 wt % concentrated solution led to low contact angles similar to those obtained with water. Nevertheless, 0.025 wt % can be considered as the optimal concentration, since on Parylene it exhibits total spreading and on the hydrophobic substrates a significant decrease of contact angle may be observed.

Silwet® L-77 surfactant, although supreme in water solutions, can be severely affected by the addition of acid. At low pH, the trisiloxane head becomes highly bipolar; thus, the solubility is enhanced and CMC is shifted towards much higher concentrations. Nonetheless, improved wetting is achievable at lower acetic acid concentration with very high surfactant concentration. At higher acid concentrations, no enhancement in wetting was observed, possibly due to the polarization of the trisiloxane head. Surface tension measurements of acidified solutions provided additional information that superspreader molecules have almost no effect on the forces that act at the liquid/gas interface. On the other hand, conventional surfactant, Triton® X-100, showed almost the same spreading behaviour as in the water-based solutions and proved to be more suitable for use in an acidic environment.

5.3 References

McMullan, P. M. (1996) *Weed Technology*, **10,** 72-77.
Sheng, G., Yang, Y., Huang, M. and Yang, K. (2005) *Environmental Pollution*, **134,** 457-463.
Snow, S. A., Fenton, W. N. and Owen, M. J. (1990) *Langmuir*, **6,** 385-391.
Vazquez, G., Alvarez, E., Sanchez-Vilas, M., Sanjurjo, B. and Navaza, J. M. (1997) *J. Chem. Eng. Data*, **42,** 957-960.
Wu, Y. and Rosen, M. J. (2002) *Langmuir*, **18,** 2205-2215.

Chapter 6 : Effect of Ageing on Trisiloxanes

In numerous practical applications of trisiloxane water-based solutions for convenience and reduced cost they are often left for lengthy periods of time in aqueous environment. Based on our findings regarding detrimental effect of low pH environment, we suspected similar mechanism may lead to the loss of their interfacial activity. Although trisiloxanes were extensively investigated (Hill, 2002) (and references therein), the potential loss of effectiveness of silicone surfactants due to ageing in aqueous environment has been somewhat overlooked. It was first mentioned in (Knoche et al., 2002) trisiloxanes can be expected to eventually lose their wetting ability in aqueous environment. Claims were made that the change in trisiloxane behaviour may appear even at short times (Stürmer et al., 1994). Yet, Hill (Hill et al., 1994) and He (He et al., 1993) did not observe any changes at short time scales. Unfortunately, although industrial and practical interest of this phenomenon is unquestionable, it did not seem to attract a lot of attention in recent years and question of ageing of trisiloxanes remained unanswered.

6.1 Ageing of Surfactant Solutions

Three specific concentrations of superspreader Silwet® L-77 and conventional Triton® X-100 surfactant were tested: the critical wetting concentration (CWC) of 0.025 wt % and one concentration both above and below it: 0.0125 wt %, which should roughly correspond to critical aggregation concentration (CAC), and 0.1 wt % as a relatively high surfactant concentration (4 CWC) and the solution can be considered as fully saturated with aggregates and freely solubilised molecules. These concentrations correspond to 1, 2 and 8 CMC for Triton® X-100. The wetting capabilities of various solutions were tested daily and assessed in terms of the equilibrium contact angle on Teflon®, on which pure water exhibits equilibrium contact angle of 120°.

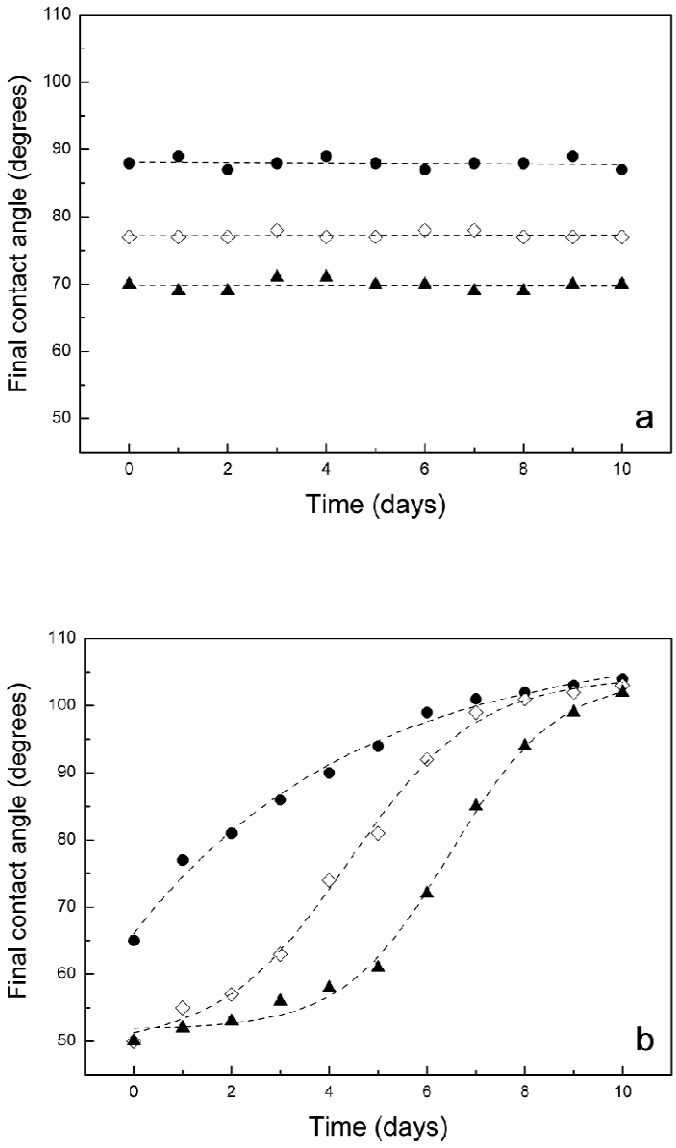


Figure 6.1 Ageing of aqueous surfactant solutions; Triton® X-100 surfactant (a) and Silwet® L-77 superspreader (b). Symbols used ●, 0.0125 wt %; ◊, 0.025 wt % and ▲ for 0.1 wt %.

The results of regular testing of wetting performance of Silwet L-77® and Triton® X-100 solutions on Teflon® surface over a number of days are presented in Figure 6.1. Final contact angles generally increased for Silwet® L-77 solutions, while for conventional Triton® X-100 surfactant no notable difference in wetting performance was observed. The continuous increase in contact angle values indicated trisiloxanes

were losing their interfacial activity. The most sudden increase was noticed for the lowest tested concentration, 0.0125 wt % within the first 24 hours, after which the angle value continued to rise almost linearly, and eventually reaching high contact angle value ~103°, exhibiting non-wetting. More concentrated solutions showed different trends. For 0.025 wt % solution major increase in final contact angle occurred after 3 days, while for 0.1 wt % solution 5 days of aging in water lead to sharp rise in contact angle. Eventually both 0.025 wt % and 0.1 wt % solutions exhibited contact angle of 103°. We suspect this is the limiting value for a given solid (Teflon®) and that reduction from the contact angle value of 120° that pure water exhibits may be attributable to the activity of the additives in commercial superspreader product. Within 10 days interfacial activity of all examined Silwet® L-77 solutions got significantly diminished and solutions of all concentrations did not exhibit contact angles lower than 103°. On the other hand, conventional Triton® X-100 surfactant wetting ability was not in any way affected by aqueous environment even for longer ageing times. Although wetting propensity of Triton® X-100 solutions was initially inferior to that of equivalent Silwet L-77® solution, but after ageing, it was superior.

6.2 Ageing Mechanism

The sensitivity of Si-O bond in the trisiloxane head to very low or very high pH has already been reported (Radulovic et al., 2009, Snow et al., 1990). If exposed to low pH environment, trisiloxanes completely lose their interfacial ability practically instantaneously. Although hydrolysation has been mentioned in the literature as the most plausible mechanism, different hydrolysation products have been suggested (Snow et al., 1990, Knoche et al., 2002, Hill, 1999). In (Hill, 1999) and references therein, authors proposed ≡Si-OH groups are formed. However, Snow et al. (Snow et al., 1990) claimed that it is hexamethyldisiloxane is more likely for to be the product (Equation 6.1):

$$2(CH_3SiO)_2SiCH_3R \rightarrow (CH_3Si)_2O + (CH_3SiCH_3R)_2O \quad \text{(R6.1)}$$

Since hydrolysation of Si-O bond in the acidic solution occurs as a result of the activity of the free protons, H^+, we suggest the same mechanism takes place in aqueous solution, at pH = 7, but on a different time-scale. The autoionisation of liquid water is known to spontaneously produce free hydronium ions after 10 hours (Eigen and de Maeyer, 1955). Additionally, various time scales have been suggested for an average lifetime of the hydronium ion (Geissler et al., 2001). Consequently, it can be expected that hydronium ions interact with the trisiloxane head in the same manner as at low pH. Formation of hydrogen bonds between $O^{\delta-}$ from the trisiloxane head and $H^{\delta+}$ from the water leads to polarisation of Si-O bond, which becomes come susceptible to nucleophilic substitution. However, the overall effect is not instantaneous, as not all trisiloxane molecules are affected at the same time. Thus, the aggregates probably act as reservoirs of the 'intact' surfactants with the hydrophobic head oriented inwards and therefore not being exposed. As solubilised surfactants undergo hydrolysation, and hence lose their interfacial activity, they are being replaced at the interfaces by fresh molecules migrating from the micelles, which are predisposed to be affected in the same manner and the process continues. Solutions studied exhibited sudden increase in final contact angle at different times, according to their concentration, that corresponds to the moment when quantity of active surfactants is insufficient to achieve the expected wetting enhancement. In order to quantify the loss of interfacial activity we have defined the degree of degradation:

$$degree\ of\ degradation = \frac{\theta_{aged_0} - \theta_0(t)}{\theta_{aged_0} - \theta_{F0}} * 100\% \quad (6.1)$$

where θ_{F0} and $\theta_0(t)$ are the equilibrium contact angles of the freshly prepared trisiloxane solutions and that tested at time, *t*, after preparation. θ_{aged_0} is set to be 103° as the limiting equilibrium value for aged superspreader solutions on the given

surface. In Figure 6.2, two prominent stages in ageing, separated by dotted lines on the graph, can be identified. The first stage corresponds to hydrolysation of the excess of freely solubilised surfactants. Thus, duration of this stage depends on the total concentration of trisiloxanes in the solution. At this stage, only the excess of free molecules is affected by the hydrolysation process. However, the overall wetting performance is still noteworthy and gradually decreasing with time as the amount of active surfactants is being reduced. As surfactants lose their interfacial activity, intact surfactants from the aggregates diffuse to the interface and enhance wetting. Nevertheless, the fresh surfactants are also subjected to hydrolysation and process continues until the quantity of the intact surfactants does not reach critical value. Once the concentration of intact molecules reaches 'critical' level, which, we believe, corresponds to CAC, the mechanism changes and loss of wetting ability progresses more rapidly.

The length of the first stage was found to be proportional to total surfactant concentration, while the second stage was very similar for all inspected concentrations. The lowest examined concentration, 0.0125 wt %, which may be considered to be just above CAC (Ivanova et al.), had very short first stage (< 1 day) and subsequent loss of wetting ability corresponds to the second stage, which seems to be a linear function of time. Solutions of the two higher surfactant concentrations exhibited the same phenomenon; once the wetting ability of solutions, which had initial concentrations equal to CWC (0.025 wt %) or above it (0.1 wt %), was weakened to the level of performance of the solution at CAC (0.0125 wt %) the same degradation mechanism took place and all solutions showed almost linear decrease of the degree of degradation with time.

Although 0.025 wt % and 0.1 wt % solutions exhibited the same equilibrium contact angle for the fresh solution, loss of wetting ability followed different dynamics for these solutions. During the first stage, both solutions demonstrated roughly exponential decrease in both contact angle and rate of degradation and similar relationship may be presumed for the decrease of overall surfactant concentration of the aged solutions. Gradually, all freely solubilised surfactants lose their interfacial

activity due to decomposition of the trisiloxane head and concentration of intact surfactants reaches CAC. This is the moment when the second stage begins and the rate of hydrolysation alters. Linear decrease in contact angle during the second stage may be contributed to the presence of the specific type of surfactant aggregates at this relatively low concentration. Leftover intact surfactant molecules are more easily accessible for free protons and therefore more susceptible to hydrolysation. Dynamics of the second stage was expected to vary for different concentrations due to the presence of products of hydrolysation. In spite of this, second stage was found to last approximately 5-6 days until absolute loss of wetting ability occurred. Eventually, decrease of interfacial and surface tensions was found to be solely due to the presence of surface active additives in the commercial superspreader product, resulting in somewhat lower contact angle, 103°, than pure water, 120°, and no trisiloxanes could be detected in the solution.

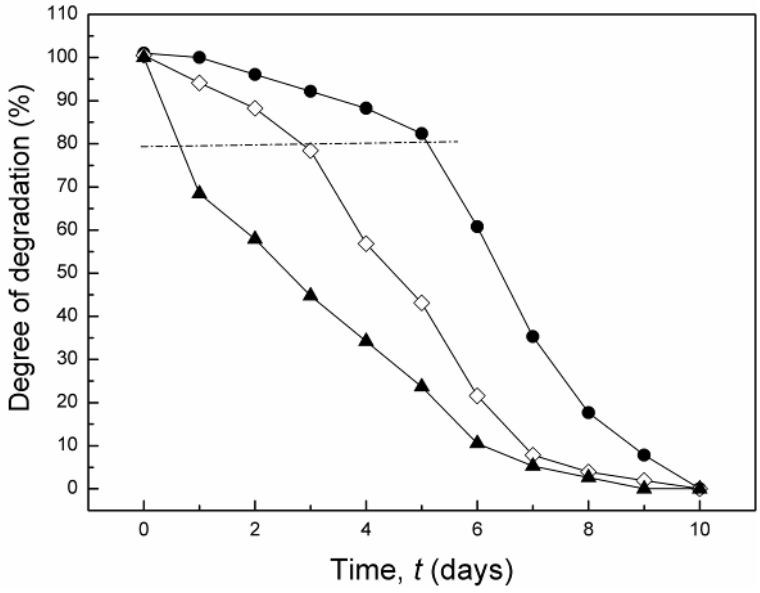


Figure 6.2 Degree of degradation of Silwet® L-77 surfactants in aqueous environment. Symbols used: (▲), 0.0125 wt %; (◊), 0.025 wt % and (●), for 0.1 wt %.

For the highest 0.1 wt % concentration the sharp rise was noticed after 5 days as the amount of present trisiloxane molecules was high enough to maintain satisfactory wetting ability, although a slight increase in contact angle value was noticed proving that the process is continuous. Hydronium attack on Si-O bond is taking place during this induction period and afterwards, when most free molecules have lost their surface activity and, at the same time, intact trisiloxane molecules come out of the micelles and get affected by hydronium ions. After this particular ageing period, there are insufficient unharmed surfactant molecules in the solution to achieve the expected vast wetting improvement and the wetting enhancement relies on the rest of surface active molecules.

6.3 Ageing Effect on Dynamics of Wetting

Results presented in Figure 6.3 prove the suggested theory. Different wetting dynamics were observed for solutions which aged for various periods compared to that of freshly prepared solutions. For 0.0125 wt % solution the same dynamics was observed for the fresh solution and the one which aged for 3 days, although the wetting enhancement was weakened, which resulted in higher contact angle value and therefore the smaller surface area was covered with the solution. However, after surfactants molecules have been in water environment for 5 days, very different behaviour was observed as typical exponential evolution was omitted. Decrease of the contact angle, started 2 seconds after deposition, was merely linear and not very effective. For solution that aged 10 days no actual decrease in contact angle was noticed as the initial value was the same as the ‘equilibrium’ one. More concentrated 0.1 wt % solution also revealed dissimilar trends for different ageing times. The solution which aged 3 days showed almost the same wetting behaviour as the fresh solution, both in dynamics and wetting enhancement. Due to larger amount of surfactants in the solution, it is necessary for such solution to age for longer time, until enough molecules endure hydrolysation and wetting capabilities weaken. For the solutions which aged for 5 and 6 days increase in final contact angle was

observed, although the specific exponential dynamics was not altered. However, change in dynamics of wetting was noticed for 7-days-old solution, similar to that observed for 5-days-old 0.0125 wt % solution, although more prominent. Eventually, both solutions which aged for 10 days performed the same – no actual decrease in contact angle value, ~ 103°. Indistinguishable behaviour observed for different ageing periods proves that the identical hydrolysation mechanism takes place in all solutions, but quantitatively this effect is reversely proportional to the amount of the surfactants in the solution. In general, more concentrated solutions were relatively immune to water environment for very short periods, while those with lower concentration started to lose their wetting capability after only 24 hours. Therefore, it may be presumed that 0.1 wt % and higher concentrated trisiloxane solutions can be considered relatively stable in water environment for a few days, although wetting dynamics may be slightly altered. Change in wetting kinetics can be explained in terms of altered diffusion mechanism by the presence of products of hydrolysation present in the solution. There is no typical exponential evolution of the contact angle and linear dependence takes place. The induction period, when contact angle is constant, is presumably due both to ongoing disaggregation as surfactants are leaving the micelles and retarded diffusion to the interface. Nevertheless, as long as there are 'enough' intact surfactant molecules in the solution to effectively adsorb at the interfaces, dynamics of trisiloxane spreading will follow expected exponential trend. Although solutions of higher concentrations were relatively stable in water environment for few days and their wetting ability was not vastly affected, the effect of ageing of trisiloxanes in aqueous environment is a very delicate issue and further investigation is necessary for optimisation of superspreaders' performance.

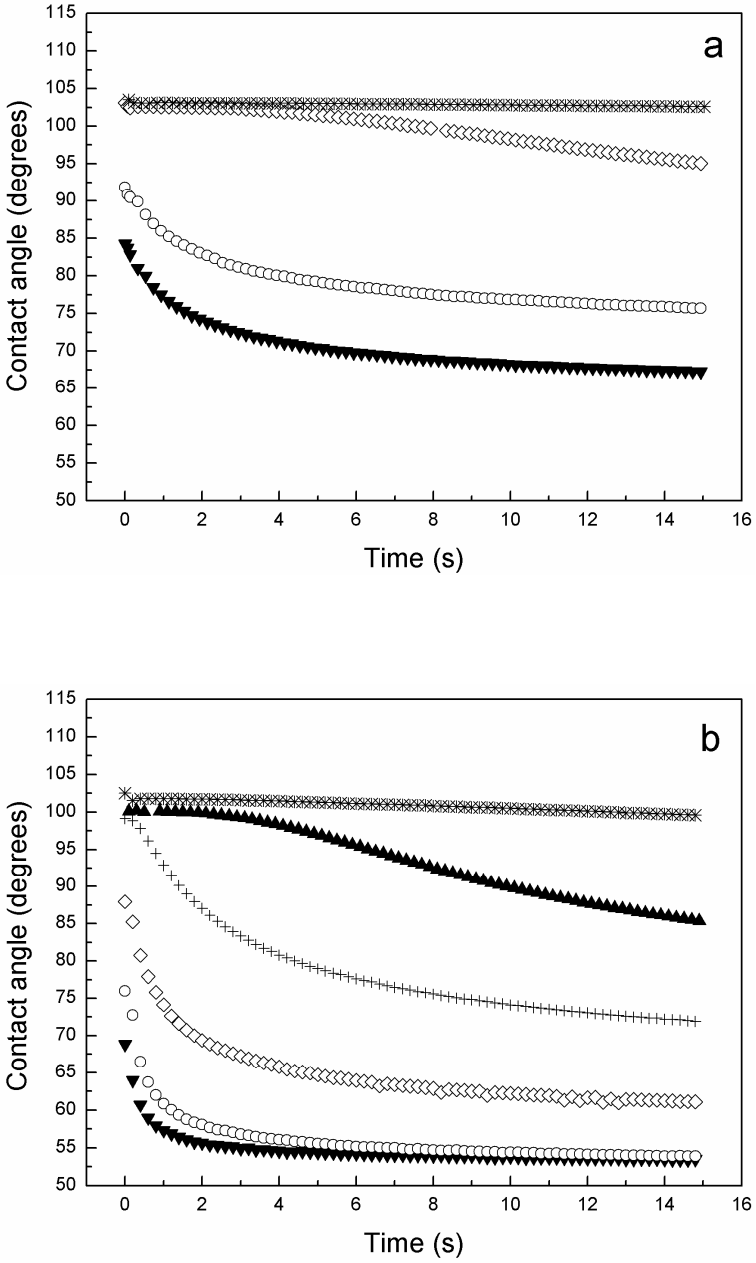


Figure 6.3 Different trends were noticed for evolution of the dynamic contact angle for various aging times for 0.0125 wt % (a) and 0.1 wt % (b) Silwet L-77 solutions. Symbols used are: ▼, fresh solution; ○, 3 days; ◊, 5 days; +, 6 days; ▲, 7 days and ∗, 10 days.

6.4 Conclusions

Effect of long-term exposure to water on trisiloxane surfactants was investigated. Unlike conventional surfactants, superspreaders gradually lost their wetting ability after a number of days depending on the total surfactant concentrations. Constant daily decrease in contact angle on hydrophobic Teflon® surface revealed molecules were losing their interfacial activity. We have quantified ageing phenomenon of trisiloxanes and suggested a probable mechanism of disintegration of 'T'-shaped surfactant head. Additionally, we showed how ageing of aqueous trisiloxane solutions alters their wetting dynamics.

6.5 References

Eigen, M. and de Maeyer, L. (1955) *Z. Elektrochem.*, **59,** 986.

Geissler, P. L., Dellago, C., Chandler, D., Hutter, J. and Parrinello, M. (2001) *Science*, **291,** 2121 - 2124.

He, M., Hill, R. M., Lin, Z., Scriven, L. E. and Davis, H. T. (1993) *J. Phys. Chem.*, **97,** 8820-8834.

Hill, R. M. (Ed.) (1999) *Silicone Surfactants*, Marcel Dekker.

Hill, R. M. (2002) *Current Opinion in Colloid & Interface Science*, **7,** 255-261.

Hill, R. M., He, M., Davis, H. T. and Scriven, L. E. (1994) *Langmuir*, **10,** 1724-1734.

Ivanova, N., Starov, V., Rubio, R., Ritacco, H., Hilal, N. and Johnson, D. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, **354,** 143-148.

Knoche, M., Tamura, H. and Bukovac, M. J. (2002) *Journal of Agricultural and Food Chemistry*, **39,** 202-206.

Radulovic, J., Sefiane, K. and Shanahan, M. E. R. (2009) *Journal of Colloid and Interface Science*, **332,** 497-504.

Snow, S. A., Fenton, W. N. and Owen, M. J. (1990) *Langmuir*, **6,** 385-391.

Stürmer, A., Thunig, C., Hoffmann, H. and Gruening, B. (1994) *Tenside Surf. Deterg.*, **31,** 90.

Chapter 7 : Binary Surfactant Mixtures of Trisiloxanes

7.1 Binary Surfactant Mixing Theory

The behaviour and performance of surfactant mixtures have been extensively studied over recent years because of their numerous applications and potentially superior properties compared to a single surfactant. The composition of mixed micelles has been considered as a key parameter in the complete understanding of aggregation mechanisms and consequently the non-ideal behaviour exhibited. Initially, in simplified models, mixed micelle structure has been treated as an ideal mixture of pure surfactants (Lange and Beck, 1973, Clint, 1975). A simple harmonic rule of mixtures of the type:

$$\frac{1}{c_M} = \frac{\alpha_1}{c_{M_1}} + \frac{(1-\alpha_1)}{c_{M_2}} \qquad (7.1),$$

has been suggested, where c_M, c_{M_1} and c_{M_2} are respectively critical micelle concentrations (cmcs) of the mixture, and pure surfactants 1 and 2, and α_1 is the molar fraction of surfactant 1 in the mixed solution. However, a need was found to adjust the above equation so that it could be applied to non-ideal systems. Rubingh (Rubingh, 1979) has introduced activity coefficients, f_1 and f_2, for each component surfactant, 1 and 2, in the mixed micelle, leading to a modified form of Equation 7.1:

$$\frac{1}{c_M} = \frac{\alpha_1}{f_1 c_{M_1}} + \frac{(1-\alpha_1)}{f_2 c_{M_2}} \qquad (7.2).$$

Furthermore the activity coefficients can be expressed as (Rubingh, 1979, Holland and Rubingh, 1983):

$$f_1 = \exp \beta_{12} (1-x_1)^2$$
$$f_2 = \exp \beta_{12} x_1^2 \qquad (7.3),$$

where x_1 is the mole fraction of surfactant 1 in the mixed micelle (*not* in the solution) and β_{12} is an interaction parameter indicating the type and intensity of interactions between surfactant molecules in the mixed micelle. For ideal mixing $\beta_{12} = 0$. A negative value of β_{12} is indicative of a stable mixed system, in which interactions between surfactant molecules are attractive. Negative values of β_{12} are often associated with synergism (Jost et al., 1988, Carnero Ruiz and Aguiar, 1999).

However, the synergistic phenomenon is not only related to specific interactions between different surfactant types (expressed by the value of parameter β_{12}), but also to the nature of individual surfactants in the mixture must also be taken into account (Rosen and Sulthana, 2001). Details of ionic surfactant systems studied and a few theoretical models for cationic/anionic, cationic/non-ionic and anionic/non-ionic mixtures, which are in excellent agreement with experimental results, can be found in the literature (Nishikido, 1992, Nishikido, 1991). Investigation of mixtures of non-ionic surfactants has generally shown that their mixing behaviour can be considered as ideal and that the simplified theory of mixed micellisation ($f_{12} = 1$) was in good agreement with experimental results (Carnero Ruiz and Aguiar, 1999, Nagarajan, 1985). Depending on the two constituent surfactants in question, ideal, antagonistic, or synergistic behaviour can be observed. The additivity rule states that the solubilization capacity X of the mixed micellar system varies linearly with the surfactant mole fraction x_i in the mixed micelle:

$$X = \sum_i x_i X_i \qquad (7.4),$$

where X_i is the solubilization capacity of the micellar system of the pure surfactant i. Depending on the solubilization capacity of the mixed micellar system, three possible cases may be observed: it may be larger, smaller or equal in magnitude to the solubilization capacity predicted by Equation 7.4. The first case is called a “positive synergistic solubilization” effect by the mixed surfactants, and the following two “negative synergistic (or antagonistic) solubilization” and “non-synergistic solubilization” effects (ideal mixing), respectively (Christian and

Scamehorn, 1995). The synergistic effect occurs as a result of the interactions of the solvent with each of the constituent surfactants and the interactions between constituent surfactants in mixed micelles. However, the number of non-ionic surfactants investigated is quite limited. Moreover, few experimental studies, which we discuss below, have been performed on superspreader mixtures.

Hill was one of the first to explore mixtures of non-ionic trisiloxane surfactants with a cationic (C_{12}TMABr), an anionic (SDS) and a non-ionic ($C_{12}(EO)_7$) surfactant (Hill, 1999). He found that non-ionic/non-ionic combinations showed antagonistic behaviour (positive non-ideal, higher cmc values than for ideal mixing), that the non-ionic/cationic combinations showed ideal behaviour, and that the non-ionic/anionic combinations showed synergistic mixing behaviour (negative non-ideal, lower cmc values than for ideal mixing). Regular solution theory failed to give an explanation of measured cmc values, which suggests that interactions between surfactants depend on the mixing ratio of the two components. Further conjecture suggested that different molecular sizes and shapes may prevent an effective packing of the two surfactant molecules in the mixed micelle: a steric effect.

Rosen and Wu have also studied mixtures of Silwet L-77® and N-pyrrolidinones (Rosen and Wu, 2001). They concluded that the adsorption of mixed surfactants at the liquid-gas (*l-g*) interface barely exhibits any enhancement compared with pure Silwet L-77® solution. Furthermore, the solution with the lowest surface tension measured at cmc concentration showed the lowest adsorption efficiency. Later, it was determined that the surface tension of the superspreader surfactant mixtures was very similar for both those exhibiting synergism and those which do not (Rosen and Song, 1996). It was also concluded that sufficiently long hydrocarbon chains, regardless of the nature of the hydrophilic group, can exhibit synergism, but at the same time, the enhancement of superspreading is not related to surface tension value (Rosen and Wu, 2001).

Nagarajan (Nagarajan, 1985) has developed a molecular theory for the formation of mixed micelles as an extension of the theory for single-component micelles. The

theory is based on the molecular thermodynamic expression for the Gibbs energy of formation of the mixed micelle, which is composition dependent, and which can be decomposed into bulk and interfacial components. He concluded that surfactant mixtures displaying markedly nonideal micellisation behaviour are those for which the interfacial interactions show significant composition dependence.

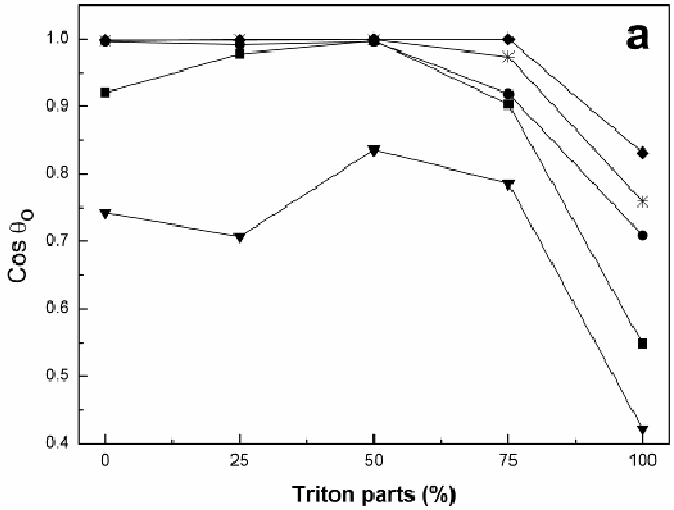
7.2 Trisiloxane-Conventional Surfactant Mixtures

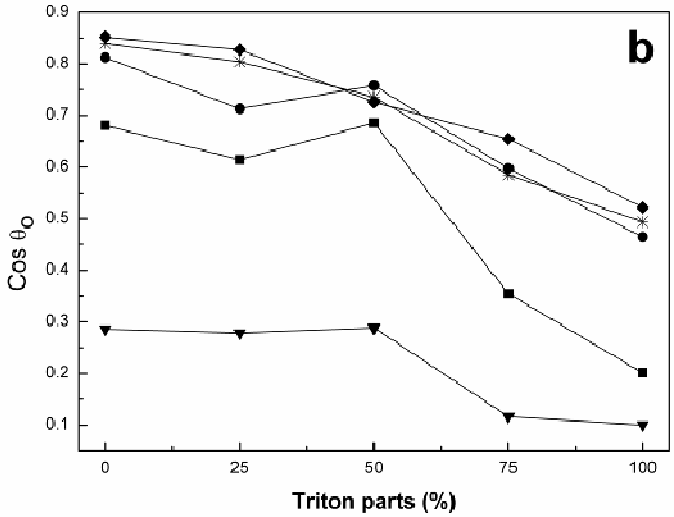
Wetting performance of aqueous binary mixtures of a superspreader, Silwet L-77® or Additive 67®, and a conventional surfactant, Triton X-100®, was investigated on hydrophobic surfaces. A range of concentrations was tested: 0.00625, 0.0125, 0.025, 0.0625 and 0.125 wt %. For each concentration, three mixing ratios were examined: 25:75, 50:50 and 75:25 (the proportion of surfactant in the mixture by weight). Results presented in Figure 4.5 suggest theoretical CMC values for the trisiloxane-based surfactants to be fairly similar to that of Triton X-100®, and therefore, the concentrations above were chosen as representative for the surfactant mixtures studied. Results corresponding to equilibrium contact angles after spreading of micro-litre drops of mixed surfactant solutions, Silwet L-77®-Triton X-100® and Additive 67®-Triton X-100®, deposited on the various polymeric substrates, are presented in Figure 7.1. It may be seen that both total surfactant concentration and hydrophobicity of the substrates were found to be major factors in the (non)ideal behaviour observed. The two surfactant mixtures studied exhibited various types of behaviour. Moreover, results obtained showed different trends on slightly hydrophilic Parylene® compared to Cytop® and Teflon®, which are hydrophobic surfaces. Both surfactant mixtures exhibited unexpected behaviour on hydrophilic Parylene®. By “unexpected”, we mean that the usual monotonic change in wettability (even if non-linear), associated with classic laws of mixtures is transgressed. As can be seen in Figure 7.1 (b) and (d), wetting capability passes through a maximum (minimum contact angle) somewhere in the middle ranges of superspreader-Triton X-100® relative proportions. This trend of obtaining better wettability for a mixture of surfactants than either alone is intriguing. On hydrophobic substrates, more

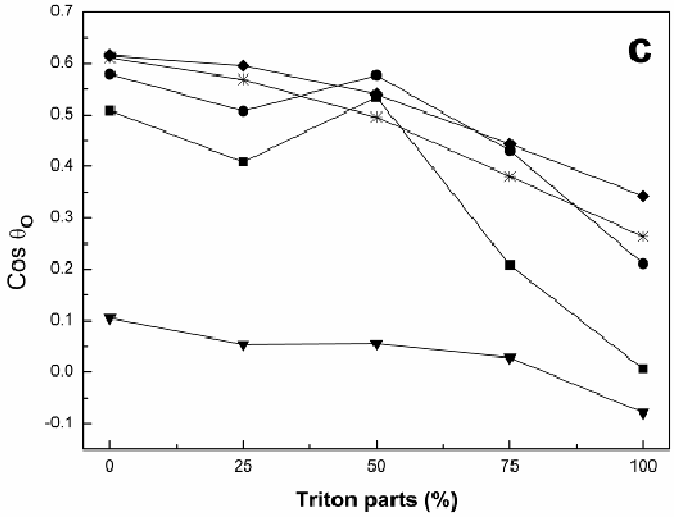
expected behaviour was noticed for all Additive 67®-Triton X-100® mixtures, while for Silwet L-77®-Triton X-100® mixtures this was clear. Lower concentration Silwet L-77®-Triton X-100® solutions (but not the lowest) sometimes exhibited "unexpected" behaviour as the final contact angle of the mixture was out of the range of final contact angle values of the pure surfactants. For higher total surfactant concentrations, above the critical concentration, the measured final contact angles implied that ideal mixing took place in the solution.

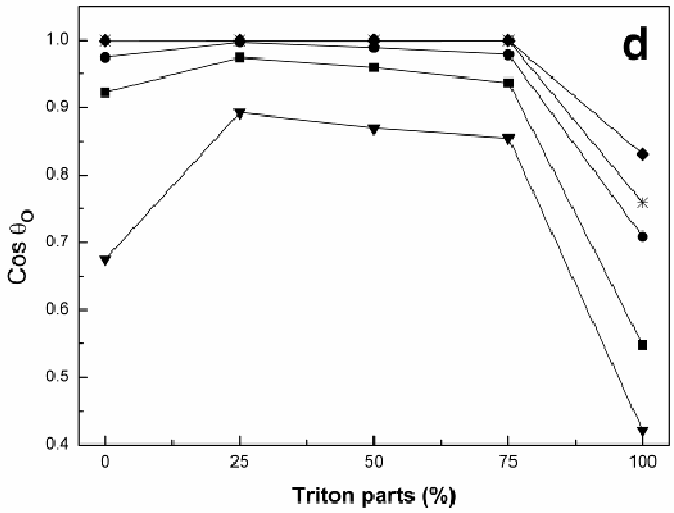
On Parylene®, the lowest contact angles were reached with 50 % Silwet L-77®-50 % Triton X-100® mixture, as shown in Figure 7.1 (a). Superiority of this particular composition was distinguished even for the lowest concentration of 0.00625 wt %: for all other concentrations total spreading was achieved ($cos\ \theta_o \approx 1$), even for 0.0125 wt % solution, although at this concentration neither Triton X-100® nor Silwet L-77® as pure surfactants exhibit total spreading. In general, greater wetting improvement was observed with mixtures with a higher amount of Silwet L-77® in the mixture. For the highest concentration examined, 0.125 wt %, the deposited drop formed a thin liquid film over the Parylene® surface for all mixing ratios, including 25 % Silwet L-77®-75 % Triton X-100®, showing the superiority of superspreader adsorption over conventional surfactant, as measured contact angle was very similar to that exhibited by pure 0.025 wt % Silwet L-77® solution. One may therefore presume that the effect of the presence of Triton X-100® molecules, at sufficiently high Silwet L-77® concentrations (above which it as pure surfactant exhibits total spreading), may be almost negligible. Unlike Silwet L-77®- Triton X-100® mixtures, for which only certain mixing ratios revealed synergistic behaviour, Additive 67®-Triton X-100® solutions showed very low contact angles on Parylene® for all mixing ratios and at all concentrations, as shown in Figure 7.1 (d). Higher concentrations exhibited total spreading for all mixing ratios, even for 0.025 wt % 25 % Additive 67®-75 % Triton X-100® mixture, which was not possible with Silwet L-77®-Triton X-100® mixture at that concentration. For lower concentrations, good synergism was also noticed for all mixing ratios as measured contact angles were significantly lower than the final contact angles of pure surfactant solutions. This synergism was more prominent for mixtures with higher Additive 67® concentration, which is expected

since superspreaders are more efficient than conventional surfactants. Nevertheless, the extraordinary effectiveness of these mixtures on hydrophilic substrates proved that ideal mixing theory failed to provide an explanation in this case.






c
Cos θo
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
-0.1
0
25
50
75
100
Triton parts (%)


d
Cos θo
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0
25
50
75
100
Triton parts (%)

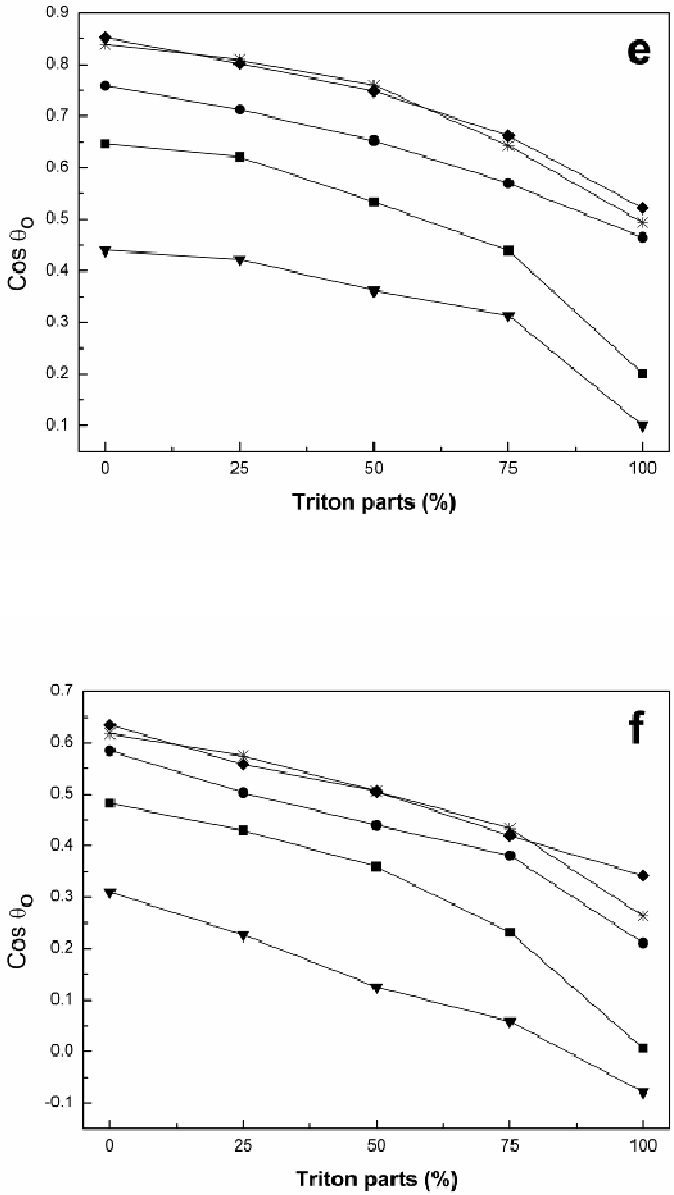


Figure 7.1 Cosine of the equilibrium contact angles of aqueous binary surfactant mixtures as a function of mixing ratio, by weight: Silwet L-77®-Triton X-100® mixtures on (a) Parylene®, (b) Cytop®, (c) Teflon® and Additive 67®-Triton X-100® mixtures on (d) Parylene®, (e) Cytop®, and (f) Teflon®. Total surfactant concentrations are ▼, 0.00625 wt %, ■, 0.0125 wt %, ●, 0.025 wt %, ∗, 0.0625 wt %, ▲, 0.125 wt %.

On hydrophobic surfaces, Cytop® and Teflon®, Silwet L-77®-Triton X-100® mixtures confirmed the trends described above. The ratio 50 % Silwet L-77®-50 % Triton X-100® proved to be matchless compared to other mixing ratios investigated. The superiority of superspreaders over the conventional surfactant was again proved, especially for lower concentrations, Figure 7.1 (b) and (c). For the two highest concentrations inspected, almost the same values were measured as the contact angle showed linear dependence on surfactant mixture composition, revealing ideal behaviour. However, Additive 67®-Triton X-100® mixtures showed ideal behaviour for all concentrations, Figure 7.1 (e) and (f). The final contact angles of the investigated mixtures were always in the range situated between the final contact angles of pure surfactants. Gradients of linear relations for high concentrations are very similar to those for Silwet L-77®-Triton X-100® mixtures for corresponding concentrations.

Measured contact angle values, which depend on effective adsorption of constituent surfactants at liquid-gas (*l*-*g*) and liquid-solid (*l*-*s*) interfaces are closely related to micellisation mechanisms. In cases where linear dependence between equilibrium contact angle and mixture composition was observed, ideal mixing behaviour may be assumed: mixed micelle formation presumably took place leading to mixed adsorption layers at the interfaces. However, due to differences in molecular chain lengths, and especially in geometry (cross-sectional area), due to shape of the hydrophobic head between Triton X-100® and trisiloxane molecules, we suspect mixed micelle formation may be problematical. For Silwet L-77®-Triton X-100® mixtures at lower total surfactant concentrations, incompatibility between dissimilar surfactant types probably promotes adsorption at the phase boundaries instead of mixed micelle formation. When the total surfactant concentration is sufficiently high, more extensive micelle formation may presumably take place simply due to the numbers present, despite steric problems, since Triton X-100® molecules in the solution act as an obstruction to effective micelle formation. When surfactants are added to the solution in equal quantities, mixed aggregation is not energetically favoured, mixed micelle formation is particularly hindered and both surfactant types

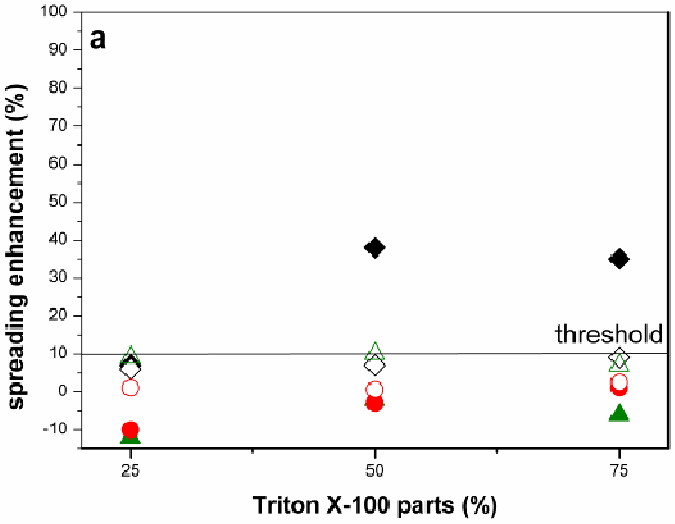
tend to stay solubilised and pack at the interfaces. Adsorption at the *l-s* interface may include a mixed surfactant monolayer with the insertion of Triton X-100® molecules in between adsorbed trisiloxanes. This may be facilitated by the smaller hydrophobic head of the conventional surfactant. Nevertheless, for sufficiently high total surfactant concentrations, it may be presumed that the concentration of single surfactant molecules is above cmc for that surfactant alone, and the possibility of single surfactant type micelle formation cannot be completely excluded as the dominant aggregation mechanism, since it is energetically more favourable. On the other hand, behaviour observed on hydrophobic substrates with Additive 67®-Triton X-100® solutions undoubtedly indicates ideal mixing, probably due to the presence of additives in the commercial Additive 67® superspreader, which act like stabilisers of mixed aggregates, decreasing the surface tension of the system. These (hypothetical) additives did not significantly influence spreading of pure Additive 67® solutions compared to Silwet L-77®, except for concentrations below the theoretical cmc, whereas Additive 67® was more effective on hydrophobic surfaces, but not on Parylene. However, impurities present may allow more efficient surfactant-enhanced spreading to take place since, at concentrations above cmc, they tend to pack inside the mixed micelles and alleviate mixed micellisation between incompatible surfactant types. This could result in ideal mixing and adsorption behaviour, especially on hydrophobic substrates. On (relatively) hydrophilic Parylene, Additive 67®-Triton X-100® addition showed an exceptional improvement in spreading. This is possibly due to the fact that, besides additives acting to facilitate and stabilise micelle formation, there is an additional driving force due to the incompatibility of (certain) impurities with hydrophilic surfaces. This in turn promotes intensive adsorption of both conventional and superspreader surfactant molecules at the interfaces.

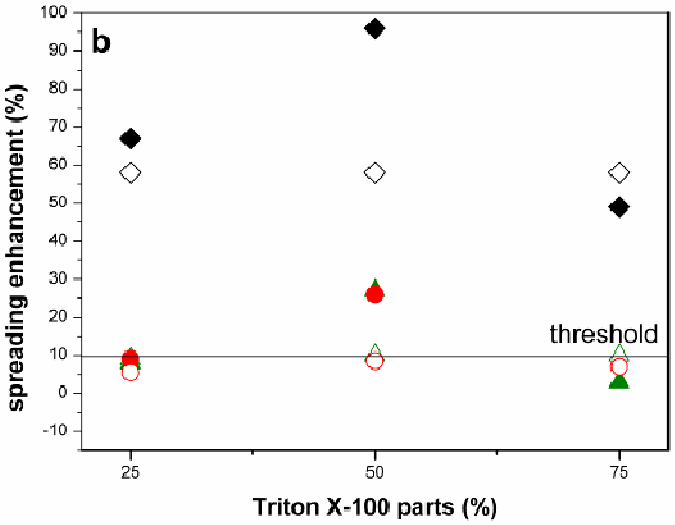
7.3 Effect of Concentration and Mixing Ratio

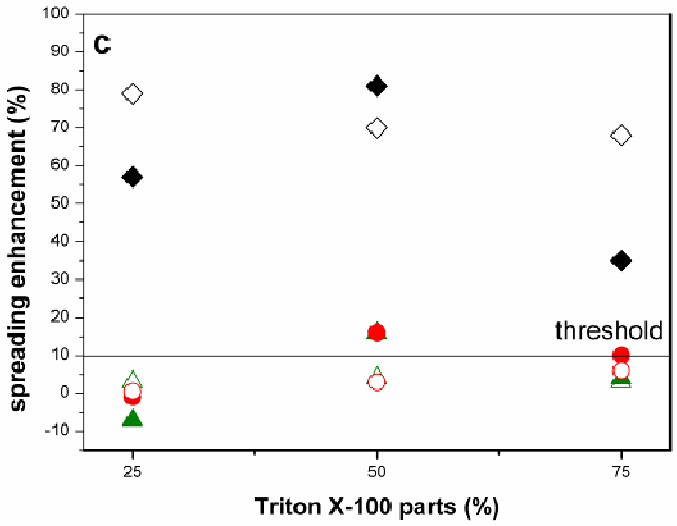
In the case of ideal micellisation, the cmc of the mixed micelle is determined only by the molar fraction of the components in the mixture (Jost et al., 1988). Supposing that ideal mixing behaviour took place in the solutions we investigated, the final contact angles of the mixtures should be proportional to the amount of each surfactant in the mixture. Measured contact angles of the mixtures considered were compared to those exhibited by single surfactant mixtures of the same concentrations. While certain mixtures showed prominent synergism, usually dependent on the mixing ratio, others exhibited weak antagonism. The intensity of the observed nonideal behaviour was quantified as the spreading enhancement, calculated using Equation 7.5:

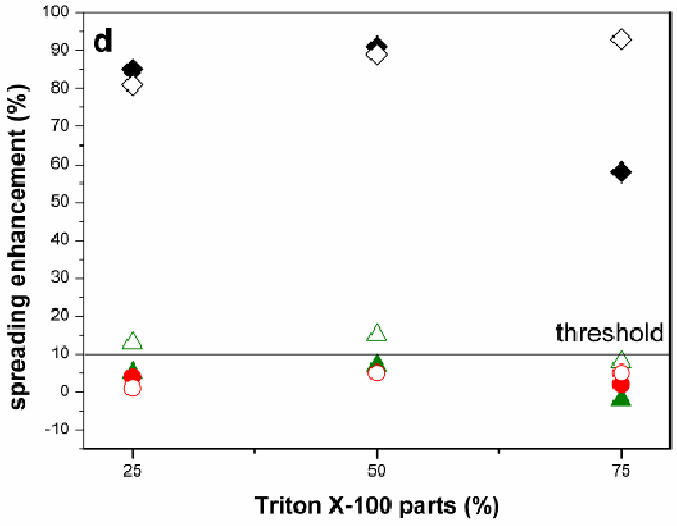
$$spreading\ enhancement\ (\%) = \frac{\theta_i - \theta_o}{\theta_i} * 100\ \% \qquad (7.5),$$

where θ_o is the equilibrium contact angle exhibited by the aqueous surfactant mixture on the solid in question, and θ_i is the estimated value of the contact angle presuming ideal mixing behaviour, which was calculated using the additivity rule (Equation 7.4), assuming solubilization capacity can be considered proportional to final contact angle value as it governs both adsorption on *l-s* and *l-g* interfaces. Observed discrepancies from the ideal mixing behaviour were denoted as synergistic or antagonistic interactions. Due to the definition of spreading enhancement (Equation 7.5), and observed variance from ideal mixing behaviour, we estimated the threshold of the spreading enhancement to be 10 %. Spreading enhancement value between -10 % and 10 % is insufficient to be considered as divergence from ideal mixing behaviour and therefore, in our analysis, only mixtures outside of this cut-off region will be discussed.


a
spreading enhancement (%)
100
90
80
70
60
50
40
30
20
10
0
-10
threshold
25
50
75
Triton X-100 parts (%)


b
spreading enhancement (%)
100
90
80
70
60
50
40
30
20
10
0
-10
threshold
25
50
75
Triton X-100 parts (%)


c
spreading enhancement (%)
100
90
80
70
60
50
40
30
20
10
0
-10
threshold
25
50
75
Triton X-100 parts (%)


d
spreading enhancement (%)
100
90
80
70
60
50
40
30
20
10
0
-10
threshold
25
50
75
Triton X-100 parts (%)

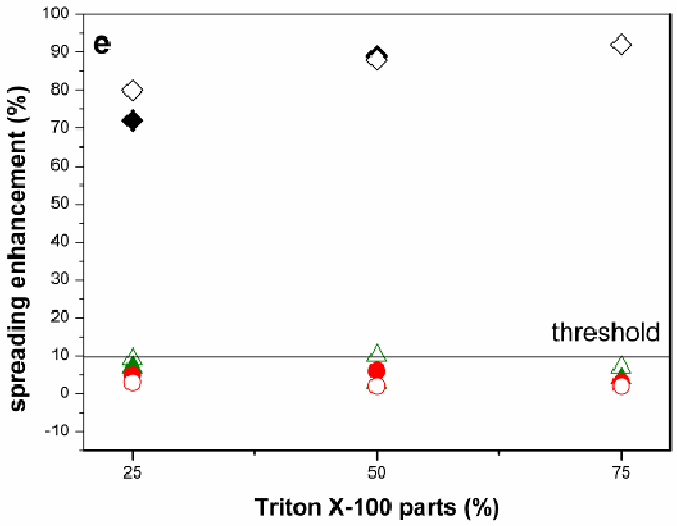


Figure 7.2 Spreading enhancement, defined by Equation 7.5, as a function of mixture composition for various concentrations: (a) 0.00625 wt %, (b) 0.0125 wt %, (c) 0.025 wt %, (d) 0.0625 wt % and (e) 0.125 wt %; solid symbols - Silwet L-77®-Triton X-100®, open symbols - Additive 67®-Triton X-100® on (◊) Parylene®, (Δ) Cytop®, (○) Teflon®.

The lowest concentration examined, 0.00625 wt %, which is known to be below cmc for each of the constituent surfactants, showed synergistic interactions only for the Silwet L-77®-Triton X-100® mixture on Parylene® for 50:50 and 25:75 mixing ratios (see Figure 7.2 (a)). We believe that this can be considered as evidence of more efficient adsorption of trisiloxane molecules at the interface, as compared to the conventional surfactant. The presence of only small amounts of Silwet L-77® appears to be capable of leading to much lower angles than predicted by ideal mixing theory. On the other hand, weak antagonism is noticed for Silwet L-77®-Triton X-100® mixtures on hydrophobic substrates, while behaviour of the Additive 67®-Triton X-100® complies with expected behaviour. Increases in concentration to 0.0125 wt % and 0.025 wt %, which we consider to be the critical values, revealed the same synergistic spreading enhancement as that of 50 % Silwet L-77®- 50 % Triton X-100® mixtures on hydrophobic substrates, while Additive 67®-Triton X-100®

solutions showed ideal behaviour on these surfaces, as presented in Figure 7.2 (b) and (c). As can be seen in Figure 7.2, the highest concentrations examined of both mixtures on Cytop® and Teflon® unveiled very similar ideal mixing behaviour, which is corroborated in Figure 7.2. On slightly hydrophilic Parylene®, both mixtures exhibited positive discrepancy, similar for all Additive 67®-Triton X-100® solutions. However, this was highest for the 50 % Silwet L-77®-50 % Triton X-100® mixing ratio. Increase in total surfactant concentration resulted in similar spreading enhancement for Silwet L-77® and Additive 67® mixtures on Parylene®. The highest examined concentrations exhibited the same variance from ideal behaviour, as shown in Figure 7.2 (d) and (e). An interesting trend was observed on Parylene for 25 % Silwet L-77®-75 % Triton X-100® solution: it showed significantly lower spreading enhancement than other mixtures for certain concentrations. This tendency can perhaps be explained by energetically unfavourable mixed micelle formation without specific additives to overcome repulsive interactions during micellisation, and thus stabilise the mixed micelles. However, as the total surfactant concentration of the mixture increases, so does the number of molecules in the system, and thus the probability of single type micelle formation is augmented. Since for this particular mixing ratio, the amount of trisiloxanes is relatively low, they will tend to adsorb at the interface, lowering the free energy of the system and thus leading to synergistic interactions, while Triton X-100® molecules will easily pack into micellar aggregates. At sufficiently high total concentrations, the amount of trisiloxanes present in the mixture is sufficiently high to allow total spreading for both mixtures, resulting in the similar spreading enhancement.

7.4 Conclusions

Wetting capabilities of the commercial superspreaders, Additive 67® and Silwet L-77®, do not greatly differ on a number of surfaces with varying hydrophobicity, once mixed with conventional Triton X-100® surfactant their performance can vary significantly. Silwet L-77®-Triton X-100® mixtures showed marked synergism only for a 50:50 mixing ratio. Antagonism, when noticed, is postulated to be related to

steric hindrance in mixed micelle formation. Ideal behaviour was only observed for high total surfactant concentrations and then only on hydrophobic surfaces.

The main difficulty for mixed micelle formation is believed to be dissimilar geometry of the hydrophobic heads of conventional and superspreader molecules. Thus, differences in chain lengths must be taken into account. The specific head geometry of Triton X-100® may also be related to a synergistic effect. The cross-sectional area of the conventional surfactant's hydrophobic head is significantly smaller than that of Silwet L-77®'s, and this reduced encumbrance therefore probably allows the 'slim' Triton X-100® molecules to insert themselves into interstices in the closely packed Silwet L-77® adsorption layer, thus achieving even greater reduction of the *l-s* interfacial tension.

Surprisingly, Additive 67®-Triton X-100® mixtures showed ideal mixing for all surfactant concentrations and all mixing ratios on hydrophobic surfaces. A proposed explanation is the beneficial effect of additives in Additive 67®, as a commercial surfactant. However, on (relatively) hydrophilic Parylene®, notable synergism was found for even for low total surfactant concentration, often leading to total spreading. Measured final contact angles were always lower than those of pure surfactant solutions. These mixtures were proven to be matchless on hydrophilic surfaces.

In order to gain better understanding of the underlying mixing mechanisms we proposed a simple theoretical model, which assumes linear variation of surface/interfacial tension with mixture composition. Undoubtedly, the physics of the spreading surfactant mixtures asks for more complex model.

7.5 References

Carnero Ruiz, C. and Aguiar, J. (1999) *Molecular Physics,* **97,** 1095-1103.
Christian, S. D. and Scamehorn, J. F. (Eds.) (1995) *Solubilization in surfactant aggregates,* Marcel Dekker.
Clint, J. H. (1975) *J. Chem. Soc., Faraday Trans I,* **71,** 1327-1334.
Hill, R. M. (Ed.) (1999) *Silicone Surfactants,* Marcel Dekker.
Holland, P. M. and Rubingh, D. N. (1983) *J. Phys. Chem.,* **87,** 1984-1990.
Jost, F., Leiter, H. and Schwuger, M. J. (1988) *Colloid & Polymer Science,* **266,** 555-561.
Lange, H. and Beck, K. H. (1973) *Kolloid Z. Z. Polym.,* **251,** 424.
Nagarajan, R. (1985) *Langmuir,* **1,** 331-341.
Nishikido, N. (1991) *Langmuir,* **7,** 2076-2082.
Nishikido, N. (1992) *Langmuir,* **8,** 1718-1723.
Rosen, M. J. and Song, L. D. (1996) *Langmuir,* **12,** 4945-4949.
Rosen, M. J. and Sulthana, S. B. (2001) *Journal of Colloid and Interface Science,* **239,** 528-534.
Rosen, M. J. and Wu, Y. (2001) *Langmuir,* **17,** 7296-7305.
Rubingh, D. N. (1979) *Solution Chemistry of Surfactants,* Plenum, New York.

Chapter 8 : Exponential Wetting of Trisiloxanes

The excellent wetting and spreading behaviour of superspreader solutions has been known and extensively studied over recent years. However, explanations for wetting dynamics and accompanying mathematical models have not yet proved completely successful. Many attempts have been made to quantify the time exponents, but none of the models so far has been able successfully to describe the whole wetting process of trisiloxane solutions, especially on hydrophobic surfaces. We have investigated partial wetting of Silwet L-77® superspreader solutions of high concentrations (well above CMC) on polymer coated substrates of varying hydrophobicity. Results obtained can be explained in terms of diffusion at the 'subsurface' as the key factor for trisiloxane enhanced wetting. A theory, involving concentration and surface tension gradients governing the dynamic wetting process, has been developed in order to explain the evolution of drop radius and consequent decrease in contact angle. The proposed model was found to be in good agreement with experimental results. Determined equation coefficients proved hydrophobicity of the substrate to be one of the crucial aspects for quality of wetting.

8.1 Effect of Substrate Hydrophobicity

Aqueous trisiloxane solutions have been tested over the years on a number of substrates of varying hydrophobicity. The reported values (Rafai et al., 2002, Lee and Starov, 2007, Nikolov et al., 2002, Radulovic et al., 2009) of wetting exponents, *n*, differed from one another although all the experiments were performed with the same superspreader solutions of the same concentration. Furthermore, all experiments mentioned were carried out under ambient conditions, temperature and pressure, and at very similar humidity. The deposited drops were approximately the same size (sufficiently small for gravity to be neglected) and had the same concentration of the trisiloxane surfactant, ~ 0.1 wt %. Moreover, the substrates on which the superspreaders were tested were ideally flat and only the hydrophobicity of the surface used varied. Therefore, we considered that it was worth investigating if the hydrophobicity of the substrate itself could be considered responsible for various

wetting exponents. Hydrophobicity and the nature of the substrate, although acknowledged to have an important role in governing the wetting process, have not been incorporated, to the best of our knowledge, in any theories so far. Reported and calculated values of *n* are presented as a function of the cosine of the equilibrium contact angle of pure water, θ_o, on the substrates used in the various experiments, used as a quantifying parameter of surface/interfacial free energy (Figure 8.1). Clearly, the value of the wetting exponent depends directly on the hydrophobicity of the substrate - the higher the hydrophobicity, the lower the exponent (Table 8.1). Some values of the exponent *n* were taken as reported by Rafai et al. (Rafai et al., 2002) and Nikolov et al. (Nikolov et al., 2002), whilst others were calculated by fitting the power law to data points presented in the publications of Rosen et al. (Rosen and Song, 1996), Ivanova et al. (Ivanova et al., 2009), Lee et al. (Lee et al., 2008) and Zhang et al. (Zhang et al., 2006), the last with the estimated contact angle of pure water on the surface of cabbage leaf. The graph also contains the exponents (open symbols) we determined by fitting the power law to the recorded evolution of drop radius on polymer surfaces of varying hydrophobicity.

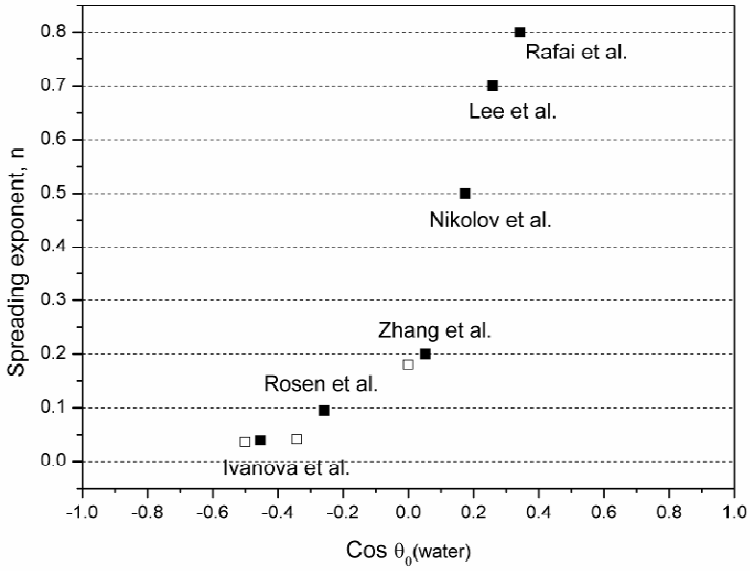


Figure 8.1 Exponents estimated by fit to $R \sim t^n$ power law for the wetting of 0.1 wt % trisiloxane drops, presented as a function of the hydrophobicity of the substrate, characterised by the equilibrium contact angle of pure water. Open symbols represent our experimental data.

Based on the trend presented above, the influence of hydrophobicity on wetting performance is unquestionable. The solid surface free energy and therefore the liquid-solid (*l-s*) interfacial tension indisputably play a major role in governing the wetting process. However, widely accepted wetting and spreading theories are lacking the parameter which could quantify this, as only the liquid-gas (*l-g*) surface tension is taken into account. In the case of wetting of surfactant solutions, the question of preference of surfactant molecules to adsorb at the *l-s* or the *l-g* interface also arises. Clearly, highly hydrophilic surfaces will not be energetically favoured by surfactant molecules as 'attractive' interactions occur between water molecules and the given solid. This generally diminishes the driving force for surfactant diffusion and adsorption. Thus, the adsorption of fewer surfactants molecules can still result in a remarkable wetting performance, due both to high efficiency superspreaders, reducing surface and interfacial tension, and high hydrophilicity of the substrate. Total spreading is observed within a few seconds if the substrate is ideally flat (no obstacles). When superspreading occurs, a thin liquid film is formed with a contact angle very close to 0° and only an increase in spreading area can be observed. Contact angle and radius are immeasurable due to complete loss of the spherical shape of the drop and its subsequent distortion. On the other hand, on highly hydrophobic surfaces, surfactant molecules will be driven to the *l-s* interface. Rapid adsorption tends to decrease the total free energy of the system, which results in improved wetting performance (Dutschk et al., 2003, von Bahr et al., 2001). This effect appears to be enhanced in the case of superspreaders. However, this is a more complex process than wetting on hydrophilic surfaces since final contact angles attained are relatively large and the overall wetting process, which lasts longer compared to the wetting process of the same solution on hydrophilic surface, can be monitored. Due to a large number of factors affecting the wetting process, the traditional power law is a vast simplification, especially when superspreaders are involved. Additionally, the power law shows a poor fit for wetting on hydrophobic surfaces. On hydrophilic substrates, the power law was verified reasonably well in early studies, as recording of wetting is quite limited by very low contact angles attained in very short times. Probably the main reason for satisfactory fits of the power law on highly hydrophobic surfaces is that fewer data points are available and

the final wetting stage, *viz*. the exponential relaxation, cannot be readily monitored. The unsuitability of the power law to describe both partial and total wetting has attracted considerable attention lately. Few attempts have been made to upgrade the power law equation or to propose new approaches. However, the majority of these are rather straightforward empirical fits, which require a basic theoretical explanation.

Table 8.1 Values and origin of reported wetting exponents, together with the corresponding list of substrates on which the wetting of 0.1 wt % trisiloxane solution was investigated.

wetting exponent	***water contact angle (°)***	***substrate***	***Origin of data/Publication***
0.8	*70*	*PET*	*Rafai et al. (2002)*
0.7	*75*	*PS*	*Lee et al. (2008)*
0.5	*80*	*PS*	*Nikolov et al. (2002)*
0.2	*87*	*Cabbage*	*Zhang et al. (2006)*
0.18	*90*	*Parylene®*	*Radulovic et al. (2009)*
0.095	*105*	*Parafilm®*	*Rosen et al. (1996)*
0.041	*110*	*Cytop®*	*Radulovic et al. (2009)*
0.039	*117*	*PTFE AF*	*Ivanova et al. (2009)*
0.036	*120*	*Teflon®*	*Radulovic et al. (2009)*

8.2 Mathematical Model

We present a theoretical model in order to provide an explanation for trisiloxane wetting behaviour on hydrophobic surfaces during the whole wetting process. Since all concentrations examined are well above CMC, we have assumed (and subsequently checked) that the vast majority of the interfacial area will have surfactant molecules adsorbed immediately after drop deposition. Surfactants are adsorbed onto the initial *l*-*g* and *l*-s interfaces, decreasing both surface and interfacial tensions to their equilibrium values. However, as wetting advances, there will be a deficit of surfactant in the surface 'layer(s)' close to the triple line, which we shall

call the ‘subsurface’, and which initiates surfactant diffusion from the ‘bulk’. In our context, the ‘bulk’ is considered to be the entire volume of the drop, with the exclusion of the subsurface. Our model assumes that, during the wetting process, the surfactant concentration at the subsurface increases in an exponentially decaying manner, due to significant diffusion of trisiloxane molecules, leading to both surface and interfacial tension gradients. The phenomenon exhibits exponential relaxation, which is a completely new approach compared to previous attempts. Exponential dependence showed an excellent fit to our experimental results and we believe it can be used successfully to describe the case of partial wetting on moderately hydrophobic surfaces. Thus, it might be the missing link between theories to date, which have not shown satisfactory agreement with experimental results, and empirically obtained models, which lack theoretical explanation.

Neglecting any gravitational contribution (valid for small drops, of dimensions typically less than the capillary length), during the initial wetting stage, immediately after the drop has been placed on the surface and new liquid-solid interface has been formed, the three interfacial tensions (γ_L, γ_S and γ_{SL}, respectively for the liquid, solid and solid-liquid surfaces/interface) acting at the triple line are unbalanced (Young’s equation is not obeyed) and wetting is driven by a tendency to reduce the total free energy of the newly formed system. This is true for any liquid, but in the case of surfactant solutions, this energy reduction involves virtually instantaneous adsorption of surfactant molecules at the *l-g* (and possibly the *l-s*) interface(s), since the concentrated solution is saturated in freely solubilised trisiloxane molecules, beside any aggregates (micelles) present. When a water-based drop is placed onto a hydrophobic surface, it is energetically favourable for surfactant molecules to adsorb at the *l-s* interface and ‘prevent’ polar water molecules from interacting with the low surface energy solid. Significantly lower initial contact angles of deposited surfactant drops, compared to those of pure water, prove that a number of surfactant molecules are very rapidly adsorbed at the interface(s). Thus, at sufficiently high surfactant concentrations (well above CMC), the initial wetting stage includes a very sharp decrease of contact angle and, consequently, an increase of the drop contact radius. The early wetting stage is very rapid and is in general agreement with the findings of

De Ruijter (De Ruijter et al., 1999). On hydrophobic surfaces, this period lasts typically only a few percent of the total wetting time, depending on the concentration, but mainly on the hydrophobicity of the substrate. Over the initially exposed surface areas, just subsequent to deposition of the drop, the *l-s* interfacial tension, along with the *l-g* surface tension, can be considered to have some surfactant adsorbed, but presumably not the equilibrium amount since the liquid has just changed its shape, with new areas exposed.

As the drop spreads, further surfactant molecules are required to adsorb both at the existent, but more importantly, also at the newly formed *l-g* and *l-g* interfaces in order to reduce surface/interfacial free energy. Here we introduce the idea of surfactant diffusion. Expansion of the interfaces leads to an effective surfactant concentration gradient between the bulk and the subsurfaces. The related chemical potential gradient leads to diffusion, which in turn modifies both surface and interfacial tensions. The local values of the latter, at the newly formed surfaces, are initially greater than at equilibrium. Surfactant adsorption modifies wetting behaviour and so, *in fine*, the latter is related to diffusion kinetics. As diffusion progresses, concentration gradients, along with surface and interfacial tensions, are being diminished. Eventually, when the subsurfaces become saturated with surfactant molecules, wetting stops since equilibrium has been reached.

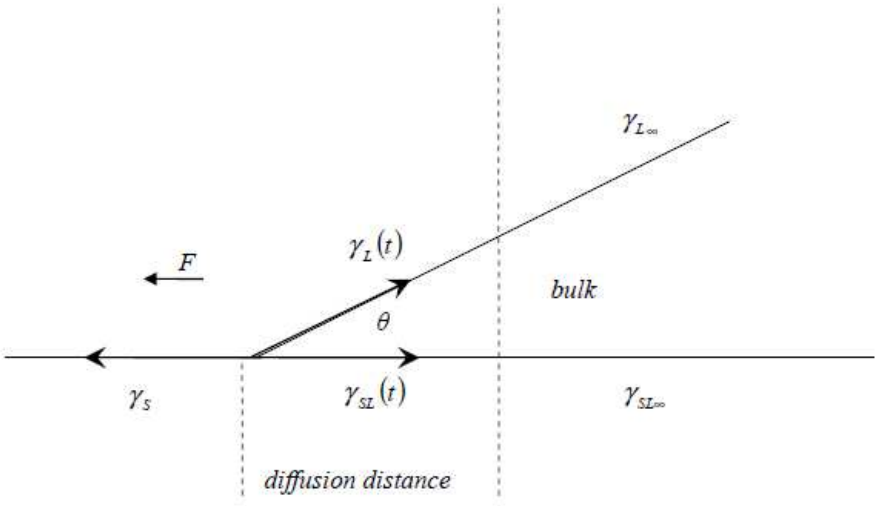


Figure 8.2 Diffusion of surfactants from the bulk to the subsurfaces diminishes interfacial and surface tension gradients and influences wetting dynamics.

8.3.1 Exponential Decay of Surface and Interfacial Tension Gradients

At sufficiently high surfactant concentrations, concentration in the bulk may be considered constant throughout the wetting process, while the surfactant concentration at both subsurfaces changes. The equilibrium values of surface concentration (saturated interface) are denoted as $C_{SL\infty}$ and $C_{L\infty}$ for *l-s* and *l-g* interfaces, respectively. Due to formation of the new surface/interface, a deficit of surfactant molecules exists in the vicinity of the triple line. Surfactant molecules in the subsurface area are considered to adsorb at both *l-s* and *l-g* interfaces, thus decreasing the concentration gradient. This in turn allows further motion of the triple line, which becomes the driving force for continuous surfactant diffusion to the subsurface. Since surfactant molecules are considered to adsorb virtually instantaneously, the wetting process is essentially diffusion-controlled, as the transfer of surfactants from the 'bulk' to subsurfaces is the rate-determining step. Displacement of the surfactant molecules from the bulk to the subsurface is characterised by a diffusion distance, *l*, which can be expressed as:

$$l \approx \sqrt{Dt_{diffusion}} \tag{8.1}$$

where $t_{diffusion}$ is the time-scale for the overall surfactant diffusion process and *D* is the diffusion coefficient of surfactant within the solution, which can be estimated from the Stokes-Einstein equation:

$$D = \frac{k\tilde{T}}{6\pi\eta\tilde{a}} \tag{8.2},$$

where *k* is Boltzmann's constant, $\tilde{T}$ is absolute temperature, η is the viscosity of the solution and $\tilde{a}$ is the molecular radius of the diffusing particle. Under ambient conditions, assuming the viscosity of the solution to be very similar to that of pure water, the diffusion coefficient is given by $D \approx 10^{-19} / \tilde{a}$, and since the molecular

radius may be estimated at $\tilde{a} \geq 20$ Å, the value of the diffusion coefficient is $D \leq 10^{-10}\,\mathrm{m}^2/\mathrm{s}$, which is in agreement with previously reported values (Rosen, 1989, Cazabat, 1994, Svitova et al., 1996). If the time-scale of wetting is approximated to a maximal value of 10 seconds, which corresponds to the total diffusion time, the diffusion distance is then:

$$l \leq \sqrt{Dt} \leq 3x10^{-5}\,m \approx 30\mu m \qquad (8.3).$$

As drop radius, *r*, is of the order of magnitude of a millimeter, we get the ratio $l/r \approx 3x10^{-2}$, suggesting that diffusion takes place in a very limited volume, or 'shell', surrounding the drop. However, it is near the triple line (≤ 3 %) that this is most important. It may be assumed that diffusional effects are local and any diffusion and/or change of concentration elsewhere inside the drop, at a radial contact distance $x \leq r - l$ may be neglected. Surfactant molecules diffuse to the subsurface where they adsorb at both *l-g* and *l-s* interfaces and the triple line advances. This diffusion is essentially perpendicular to the surface/interface, and therefore to the direction of liquid flow during wetting. Diffusion to the subsurface and surfactant adsorption continues until equilibrium is reached. Both surfactant concentrations, and therefore surface and interfacial tensions, are considered to be solely diffusion controlled near the triple line. The relaxation time, τ, is essentially independent of the release rate of surfactants from the micelle into the bulk, as total surfactant concentration is well above CMC, and therefore τ is only diffusion dependent. Diffusion may be approximated by first order kinetics, since the 'driving force' corresponds to relative surface depletion. It is convenient to define relative concentrations of surfactant at the *l-g* surface and *l-s* interface, $\tilde{C}_L(t) = C_L(t)/C_{L\infty}$ and $\tilde{C}_{SL}(t) = C_{SL}(t)/C_{SL\infty}$ where $C_L(t)$ and $C_{SL}(t)$ are the actual concentrations, giving:

$$\frac{\partial \tilde{C}_L(t)}{\partial t} = \frac{1}{\tau}\left(1 - \tilde{C}_L(t)\right) \qquad (8.4),$$

where τ is the relaxation time needed for the diffusion, leading to the standard expression:

$$\tilde{C}_L(t) = 1-(1-\tilde{C}_{L0})\exp(-t/\tau) \quad (8.5),$$

where $\tilde{C}_{L0}$ is the initial value of $\tilde{C}_L(t)$. During diffusion, there will be some 'stretching' of the liquid surface, but this effect should be minor for the following reasons. Near t = 0, although surface strain rate will be (relatively) significant due to faster wetting, $\tilde{C}_L(t)$ will be small, thus little affecting equation (8.4). For more advanced t, $\tilde{C}_L(t)$ becomes larger. However, wetting, and therefore surface strain rate are much reduced.

Taking as an approximate expression for liquid surface tension the following relation:

$$\gamma_L \approx \tilde{C}_L\gamma_{L\infty} + (1-\tilde{C}_L)\gamma_{L0} \quad (8.6),$$

where γ_{L0} and $\gamma_{L\infty}$ represent respectively the pure liquid (water) and equilibrium values of γ_L, we obtain an expression for diffusion-dependent liquid surface tension:

$$\gamma_L(t) = \gamma_{L\infty} + \Delta\gamma_L(1-\tilde{C}_{L0})\exp\left(\frac{-t}{\tau}\right) \quad (8.7),$$

where $\Delta\gamma_L = (\gamma_{L0} - \gamma_{L\infty})$.

Bearing in mind the size of the subsurface, the time constant, τ, is expected to have approximately the same value for the *l-g* and the *l-s* adsorption, since the probability that surfactant molecule will adsorb to either of the interfaces at the subsurface is similar: they are approximately equally distant. Therefore, a similar expression exists for the *l-s* interfacial tension, $\gamma_{SL}(t)$:

$$\gamma_{SL}(t) = \gamma_{SL\infty} + \Delta\gamma_{SL}(1-\tilde{C}_{SL0})\exp\left(\frac{-t}{\tau}\right) \quad (8.8),$$

where $\Delta\gamma_{SL} = (\gamma_{SL0} - \gamma_{SL\infty})$. Now, near the triple line, where diffusion takes place, fluid motion is driven by the imbalance of surface/interfacial tensions that act on the interfaces (Figure 8.2):

$$F = \gamma_S - \gamma_{SL} - \gamma_L \cos\theta \quad (8.9).$$

The wetting force changes with time according to the change of its constituent tensions, described by equations (8.7) and (8.8), leading to:

$$\begin{aligned} F &= \gamma_S - \gamma_{SL\infty} - \Delta\gamma_{SL}(1-\tilde{C}_{SL0})\exp\left(\frac{-t}{\tau}\right) - \gamma_{L\infty}\cos\theta - \Delta\gamma_L(1-\tilde{C}_{L0})\exp\left(\frac{-t}{\tau}\right)\cos\theta \\ &= \gamma_{L\infty}(\cos\theta_\infty - \cos\theta(t)) - (\Delta\gamma_{SL} + \Delta\gamma_L\cos\theta(t))\exp\left(\frac{-t}{\tau}\right) \end{aligned} \quad (8.10),$$

where use has been made of Young's equation for the equilibrium situation.
The friction force that opposes the triple line motion is:

$$F_{friction} = \frac{3\eta L U}{\theta} \quad (8.11),$$

where L is the logarithm of the ratio of a macroscopic distance, of the order of the contact radius in the case of a sessile drop, and a microscopic cut-off distance near the triple line and U is the speed of the triple line (De Gennes, 1985). (The denominator on the right should be perhaps expressed more exactly as sin θ, but this is of no consequence for the following.) The wetting velocity can be expressed as $U = dr/dt$ and since viscosity and cut-off distance in equation (8.11) are considered to be approximately constant, by combining these two expressions, we obtain:

$$F = \frac{3\eta l}{\theta}\frac{dr}{dt} = \gamma_{L\infty}\left(\cos\theta_{\infty} - \cos\theta\right) - \exp\left(\frac{-t}{\tau}\right)\left(\Delta\gamma_{SL}\left(1-\tilde{C}_{SL0}\right) + \Delta\gamma_{L}\left(1-\tilde{C}_{L0}\right)\cos\theta\right) \quad (8.12).$$

The above equation cannot apparently be solved analytically. Nevertheless, it provides valuable insight into the underlying mechanism of wetting of trisiloxane solutions, by clearly defining two key elements in the 'motor' force for wetting. The first term comes from the well-known de Gennes wetting theory (De Gennes, 1985) and presents the standard capillary (hydrodynamic) 'motor'. The latter term introduces an exponential component due to diffusion processes, which is associated with the presence of trisiloxane surfactants in the solution. Indeed, the exponential term, which illustrates diffusion, initially acts as a barrier for rapid wetting. Since diffusion to the surface, postulated above as the limiting step, can be modelled as an exponential relaxation (rate of migration is proportional to concentration gradient), it is reasonable to expect that wetting kinetics will involve similar relaxation times.

The driving force for wetting of pure liquids is the imbalance of capillary forces acting at the triple line, or so-called hydrodynamic motor (equation (8.9)). A homogeneous liquid drop has the same surface tension throughout the drop and therefore wetting is not diffusion related. Since no diffusion takes place, the wetting process can be modelled by using only the first term from equation (8.12). This case of wetting behaviour, assuming the drop of pure solvent (water) is deposited on a particular substrate, will have driving force (per unit triple line length) to wet the surface expressed as:

$$F = \gamma_{W}\left(\cos\theta_{W\infty} - \cos\theta(t)\right) \quad (8.13),$$

where suffix *W* refers to water. The simplified solution of this standard capillary/hydrodynamic scenario suggests a scaling relation of the form $r \sim t^{1/10}$, for a final contact angle of zero (De Gennes, 1985) and/or for wetting far from equilibrium $\left(\theta(t) >> \theta_{\infty}\right)$. Pure water, being of low viscosity, reaches maximal wetted area after a very short time (Marmur, 1983, Summ et al., 1987), estimated here as *ca*. 0.1 second,

being experimentally immeasurable with any precision in the present case. Hereafter, r remains constant (= $r_{W\infty}$). These two regimes are represented by curve (a) in Figure 8.3, the former as a dotted line since clearly the 1/10 power law is not justifiable right up to equilibrium, and the latter given since $r_{W\infty}$ is readily obtained experimentally.

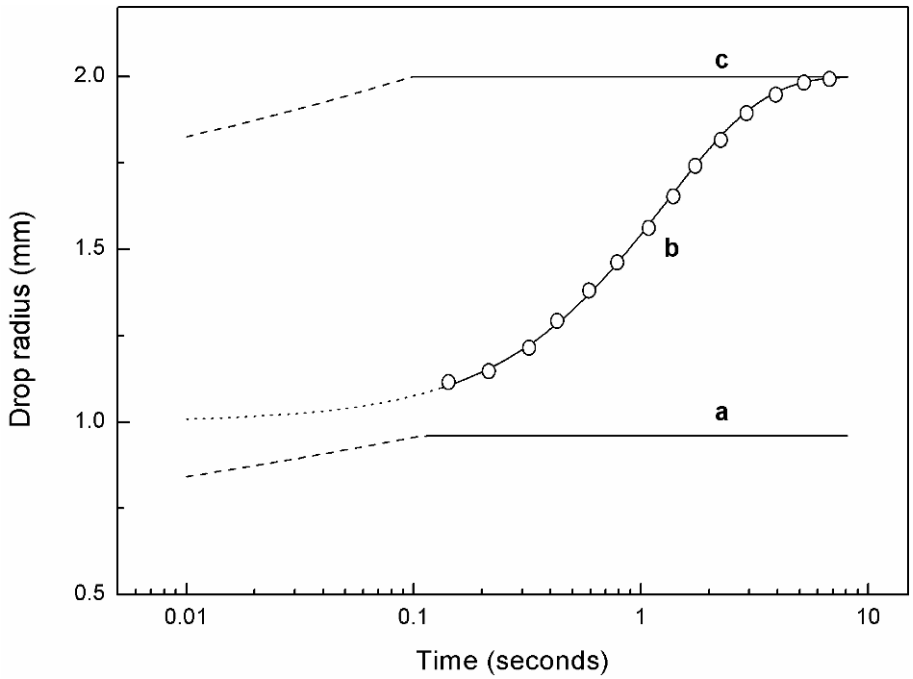


Figure 8.3. Evolution of drop radius for two extreme wetting cases compared to experimentally determined wetting performance of trisiloxane solution: (a) pure liquid with zero-diffusion; (b) experimental data for 0.025 wt % trisiloxane solution on Cytop®; (c) hypothetical case of surfactant solution with 'instantaneous' diffusion. Open symbols represent experimental data points.

For superspreader solutions, additional forces acting are caused by differences in surfactant concentrations at the interfaces, in the vicinity of the triple line, $C_{SL}(t)$ and $C_L(t)$, which cause surface/interfacial tension gradients and initiate diffusion (second term on right hand side in equation (8.12)). Due to surfactant adsorption at the expanding interface, there is a lack of surfactant molecules (compared to equilibrium) at the subsurface and therefore significant diffusion takes place from the 'bulk' to the triple line. Surfactant diffusion is, therefore, the rate-determining step,

which results in an increase of concentration at the subsurface and, consequently, decrease of relevant tensions, until equilibrium values are reached. Thus, the overall wetting behaviour can only be successfully described if both effects are taken into account. This is in agreement with our experimental results, shown in Figure 8.3 as curve (b). The extrapolated initial value of radius, r_0, is simply an estimate, since not obtainable experimentally.

In the hypothetical case, where diffusion of surfactant molecules to the subsurface could be considered 'instantaneous', diffusion would not slow down the wetting process. Hence, the second term on the right of equation (8.12) could again be neglected. The surface/interfacial tensions of the system, where diffusion takes place 'instantaneously' may be considered as constant. The driving force for wetting in this hypothetical case would then be described by a modified form of equation (8.13):

$$F = \gamma_{L\infty}\left(\cos\theta_{\infty} - \cos\theta(t)\right) \qquad (8.14).$$

The expected behaviour in this case is represented by curve (c) in Figure 8.3, using the same treatment as for curve (a) but, of course, with the correct equilibrium contact radius (r_{∞}), for the surfactant-laden liquid. This 'idealised' solution would have the same overall wetting performance as the real solution (same equilibrium contact angle and final drop radius) but following completely different wetting kinetics since, according to equation (8.14), it can be treated as a homogeneous (pure) liquid. Thus, curve (c) has a similar shape to curve (a), since the hypothetical surfactant solution would also exhibit very rapid wetting, lasting only until interfacial forces balance out.

The experimentally verified evolution of a trisiloxane drop radius is compared to the two extreme cases, presented in Figure 8.3. In the experimental case (curve (b)), the system starts near curve (a) and gradually evolves towards case (c). According to equation (8.12), the motor for surfactant wetting, F, is initially limited by the diffusion term, since $\exp\left(\frac{-t}{\tau}\right) \sim 1$. However, the overall driving force for wetting is

greatest at the very beginning, due to the highest contact angle value, which augments the first term. As wetting continues and the triple line advances, the second term decreases with time, $\exp\left(\frac{-t}{\tau}\right) \to 0$. Moreover, the first term also decreases, as the contact angle approaches its equilibrium value. Eventually, the driving force reaches zero and the wetting process ends, with no noticeable variation of (final) wetting parameters. The 'superspreading' phenomenon is thus attributed to what amounts to a change of regime of wetting conditions, with improved wetting occurring following the diffusion of surfactant molecules. It is worth emphasizing that due to the $-\Delta\gamma_{SL}\exp\left(\frac{-t}{\tau}\right)$ term in the motor, the improvement in wetting is more marked on surfaces of higher hydrophobicity, simply because $\Delta\gamma_{SL}$ is that much bigger. However, dependence of the wetting exponent, *n*, is at present too difficult to be predictable.

8.3 Validation of the Model

The wetting performance of concentrated Silwet® L-77 solutions was tested on two hydrophobic surfaces, Cytop® and Teflon®. As expected, all three solutions investigated, 0.025, 0.0625 and 0.125 wt %, which correspond to 1, 2.5 and 5 CWC (Ivanova et al., 2010), or accepting a molecular weight of 624 for the surfactant, as 4 x 10^{-7}, 1 x 10^{-6} and 2 x 10^{-6} moles/cm^3, respectively, reached the same final contact angle, the limiting value for the given solid. In our experiments, drops of similar volumes were deposited and the final wetting area was the same for all three solutions as the final drop radius values were identical, despite differences in concentration. However, the increase in concentration significantly influenced the dynamics of the wetting process. Solutions with higher trisiloxane content needed less time to reach final contact angles and their maximal drop radius. Experimental results of the evolution of the drop radius and decay of the contact angle in time are presented in Figures 8.4 and 8.5, respectively.

A sharp increase of the drop radius and decrease of the contact angle were noticed in the initial wetting stage. The intermediate wetting stage is characterised by relatively moderate increase in drop radius, followed by exponential relaxation at the very end of the wetting process. The overall evolution of the drop radius during the wetting process was found to be successfully described by using the relatively simple exponential function:

$$r(t) = r_{\infty} - a\exp(-t/\tau) \qquad (8.15).$$

Values of the coefficients a and τ depend on the properties of the solution (type and nature of surfactant, total surfactant concentration) and the surface (hydrophobicity) involved, which dictate the wetting dynamics. The drop radius will increase as the drop spreads over the surface driven by the wetting motor (equation (8.12)) until the final value is reached. The physical meaning of the coefficient a can be easily understood from the initial conditions: $t = 0;\ r = r_0 \rightarrow a = r_{\infty} - r_0$, where r_0 is the initial and r_{∞} the final (equilibrium) drop radius. The exponential function was also found to be a satisfactory model for evolution of the contact angle of the trisiloxane drops on hydrophobic surfaces:

$$\theta(t) = \theta_{\infty} + b\exp(-t/\tau) \qquad (8.16)$$

where θ_{∞} is the final contact angle value, with coefficient b being the difference between the initial and final contact angle value, $b = \theta_0 - \theta_{\infty}$.

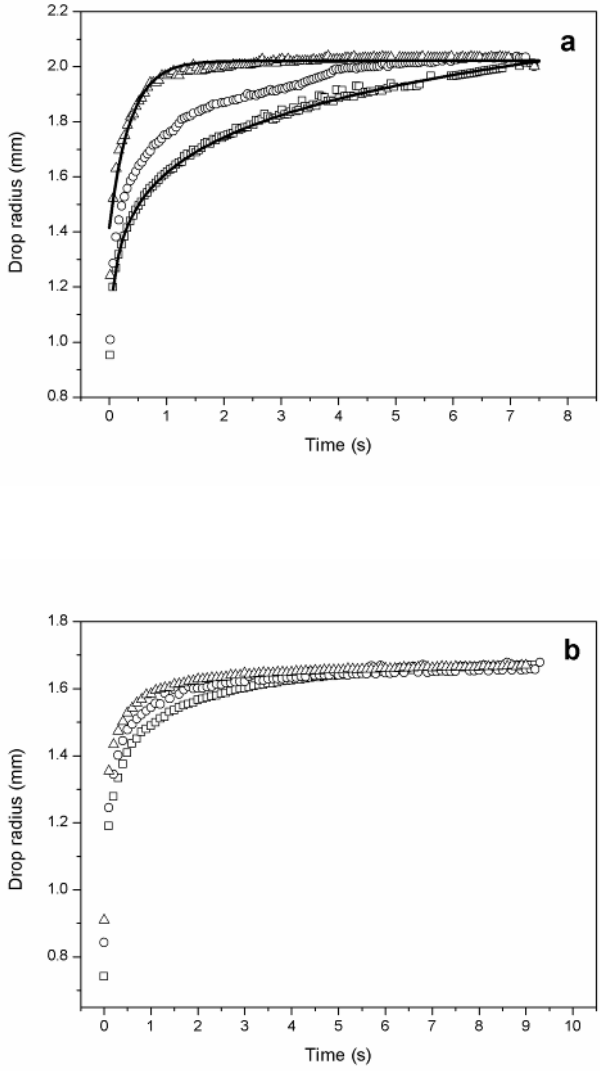


Figure 8.4 Effect of increasing trisiloxane concentration on dynamics of wetting and evolution of drop radius on (a) Cytop®, (b) Teflon®: □, 0.025 wt % (0.5 CWC); ○, 0.0625 wt % (1.25 CWC); Δ , 0.125 wt % (2.5 CWC), with black lines fitted using equation (8.15).

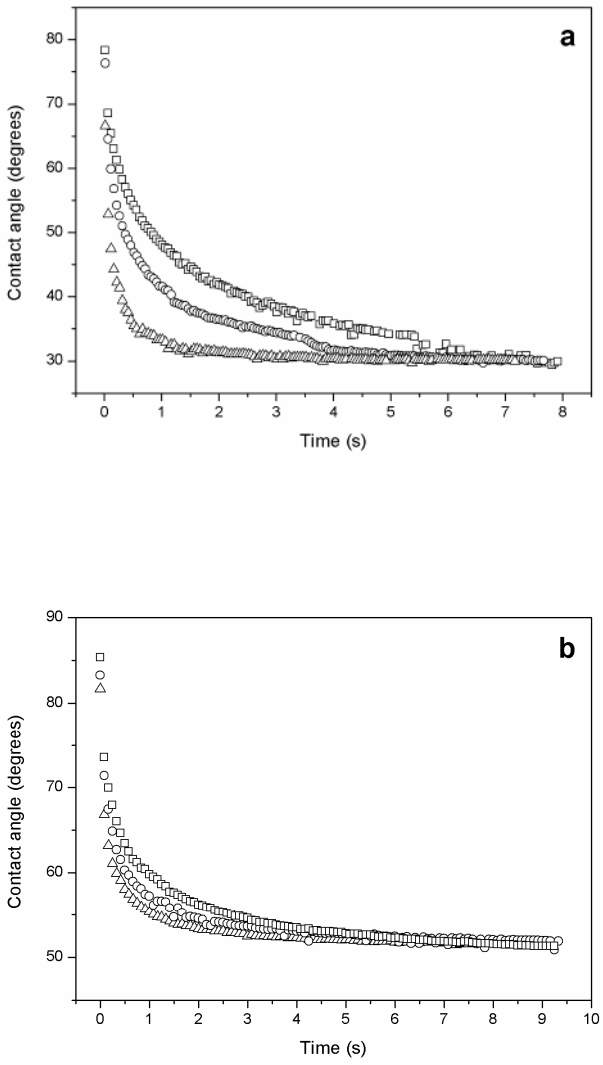


Figure 8.5 Effect of increasing trisiloxane concentration on rapidity of contact angle decay on (a) Cytop®, (b) Teflon®: □, 0.025 wt % (0.5 CWC); ○, 0.0625 wt % (1.25 CWC); Δ , 0.125 wt % (2.5 CWC).

Although equation (8.12) has no apparent analytical solution, we may derive an approximate asymptotic solution for the end stage of wetting. Equation (8.12) may be considerably simplified for the regime towards the end of wetting, as $r \to r_\infty$ and $\theta \to \theta_\infty$. Using the approximation for drop volume *V*, $V \approx \pi r^3 \theta / 4$, for relatively small contact angles ($\theta \le ca.1$ radian as is the case here in the final stage), we may rewrite equation (8.12) as:

$$\frac{dr}{dt} \approx \left(\frac{4V}{\pi}\right)^3 \frac{\gamma_{L\infty}}{\eta L r_\infty^{10}} \left(r_\infty - r\right) - \frac{4V(\Delta\gamma_{SL}(1-\tilde{C}_{SL0}) + \Delta\gamma_L(1-\tilde{C}_{L0})\cos\theta_\infty)}{3\pi\eta L r_\infty^3} \exp\left(\frac{-t}{\tau}\right) \quad (8.17),$$

or alternatively as:

$$\frac{dr}{dt} \approx \frac{\left(r_\infty - r\right)}{T} - \phi \exp\left(\frac{-t}{\tau}\right) \quad (8.18),$$

where:

$$\frac{1}{T} = \left(\frac{4V}{\pi}\right)^3 \frac{\gamma_{L\infty}}{\eta L r_\infty^{10}} = \frac{\gamma_{L\infty}\theta_\infty^3}{\eta L r_\infty} \quad (8.19),$$

and:

$$\phi = \frac{4V(\Delta\gamma_{SL}(1-\tilde{C}_{SL0}) + \Delta\gamma_L(1-\tilde{C}_{L0})\cos\theta_\infty)}{3\pi\eta L r_\infty^3} = \\ = \frac{\theta_\infty(\Delta_{SL}(1-\tilde{C}_{SL0}) + \Delta\gamma_L(1-\tilde{C}_{L0})\cos\theta_\infty)}{3\eta L} \quad (8.20).$$

Equation (8.18) may be treated as follows. Setting $\phi = 0$ (or, alternatively, $\tau = 0$), we have a standard exponential decay as a solution to equation (8.18):

$$r(t) = r_\infty - \Lambda \exp(-t/T) \quad (8.21),$$

where Λ depends on the initial drop radius at $t = 0$ (cf. the term a in equation (8.15)). Allowing ϕ and τ to be non-zero, equation (8.18) may be written as:

$$\exp\left(\frac{-t}{T}\right)\frac{d(r\exp(t/T))}{dt} = \frac{r_\infty}{T} - \phi\exp\left(\frac{-t}{\tau}\right) \quad (8.22),$$

which has the solution:

$$r(t) \approx r_\infty - \Lambda\exp(-t/T) - \frac{\phi\tau T\exp(-t/\tau)}{(\tau - T)} \quad (8.23),$$

where, again, Λ is a constant depending on contact radius at $t = 0$. Wetting kinetics is 'perturbed' by the diffusion term involving time constant τ.

Table 8.2 Coefficients obtained by fitting the function described by equation (8.15) to the evolution of drop radius. Experimental data from Figure 8.4.

Bulk surfactant conc.		***Cytop®***				***Teflon®***			
wt %	*B, (mole cm^{-3})*	*r_∞ (mm)*	*a(mm)*	*τ (s)*	*$\tau^{-1/2}(s^{-1/2})$*	*r_∞ (mm)*	*a(mm)*	*τ (s)*	*$\tau^{-1/2}(s^{-1/2})$*
0.025	*4 x 10^{-7}*	*2.02*	*0.747*	*2.52*	*0.63*	*1.65*	*0.514*	*1.12*	*0.94*
0.0625	*1 x 10^{-6}*	*2.00*	*0.649*	*1.14*	*0.94*	*1.64*	*0.434*	*0.54*	*1.36*
0.125	*2 x 10^{-6}*	*2.01*	*0.582*	*0.42*	*1.54*	*1.68*	*0.421*	*0.46*	*1.47*

Table 8.3 Coefficients obtained by fitting function, described by equation (8.16), to the evolution of contact angle. Experimental data from Figure 8.5.

Bulk surfactant conc.		***Cytop®***				***Teflon®***			
wt %	*B, (mole cm^{-3})*	*θ_∞ (°)*	*b (°)*	*τ (s)*	*$\tau^{-1/2}(s^{-1/2})$*	*θ_∞ (°)*	*b (°)*	*τ (s)*	*$\tau^{-1/2}(s^{-1/2})$*
0.025	*4 x 10^{-7}*	*30.6*	*34.2*	*2.05*	*0.70*	*52.1*	*21.2*	*1.14*	*0.94*
0.0625	*1 x 10^{-6}*	*30.3*	*30.2*	*1.09*	*0.96*	*52.5*	*20.7*	*0.63*	*1.26*
0.125	*2 x 10^{-6}*	*30.4*	*27.2*	*0.35*	*1.69*	*52.1*	*18.0*	*0.52*	*1.39*

We can thus see that the final stage of wetting is governed by the sum of two exponential decay terms. Judging by the form of equation (8.23) and Figure 8.3, we infer that $\tau > T$, i.e. that the diffusion process is intrinsically slower that the basic capillary wetting. This is hardly surprising given the form of curve (b) in Figure 8.3, as wetting apparently 'waits' for diffusion. Let us consider these results in more detail. From a qualitative point of view, we observe that, although the *final* drop radius was the same for all solutions investigated, as drops of the same volume were deposited (Figure 8.4), the coefficient *a* in equation (8.15) [or *b* in equation (8.16)] was found to decrease with increasing concentration. The higher the total surfactant concentration, the better is the wetting performance, even in the initial stage, as there are more dispersed surfactant molecules in the solution, which can readily diffuse and adsorb at the interface. Coefficients *a* and *b* consequently decrease as solutions of higher concentration had larger initial drop radius. It also depends on the hydrophobicity of the substrate and, as expected, is higher for less hydrophobic substrates. This is in agreement with the values of the coefficients obtained by fitting the functions described by equations (8.15) and (8.16) to our experimental data (Tables 8.2 and 8.3).

Let us be more quantitative. As shown by equations (8.15) and (8.16), and Figures 8.4 and 8.5, exponential decay of spreading is observed experimentally. Consider the classic hydrodynamic description towards the end of spreading (De Gennes, 1985). Referring to the treatment above and assuming, for now, that suffixes indicate equilibrium conditions since the end stages of wetting are in question, equation (8.12) simplifies to:

$$F = \frac{3\eta l}{\theta}\frac{dr}{dt} = \gamma_{L\infty}\left(\cos\theta_{\infty} - \cos\theta(t)\right) \qquad (8.24),$$

since the complicating factors due to adsorption are now absent, by hypothesis. Equation (24) may be linearised [*cf.* equations (8.17) and (8.18)], and with the time constant $T = \eta L r_{\infty} \big/ (\gamma_{L\infty}\theta_{\infty}^{3})$ [*cf.* equation (8.19)], we obtain:

$$r_\infty - r(t) \approx const.\exp(-t/T) \quad (8.25),$$

which is analogous to equation (8.15), except that the time constant is *T*, and formally the same as equation (8.21). It can similarly be shown for the contact angle dependence that [*cf.* equation (8.16)]:

$$\theta(t) - \theta_\infty \approx const.\exp(-t/T) \quad (8.26).$$

We shall apply equations (8.25) and (8.26) to the later stages of spreading towards equilibrium since the phenomenological relation holds well. The liquids used are essentially water (≥ 99.875 %), and so the viscosity, η, may be taken as *ca*. 10^{-3} Pa.s and L ≈ 10. For our results, respectively on Cytop® and on Teflon®, $r_\infty \approx$ 2 and 1.6 mm and $\theta_\infty \approx$ 0.5 and 0.9 radian. In addition, a reasonable estimate for $\gamma_{L\infty}$, after surface saturation of the water by surfactant, is *ca*. 20 mNm^{-1}. These values lead to estimates of *T*, respectively on Cytop® and on Teflon®, of ca. 8×10^{-3} and 1×10^{-3} seconds. They are 2 to 3 orders of magnitude smaller than the values of τ in Tables 8.2 and 8.3. It would therefore seem a safe assumption that the values of τ reported from experiments, found in Table 8.2 and 8.3, are *not* due to exponential decay of spreading rate expected simply from the decreasing capillary effect of a pure liquid as it approaches equilibrium. Also, the parameters in the time constant, *T*, are essentially independent of surfactant concentration, whereas experimental results show a distinct dependence. As expressed above, a reasonable hypothesis is that these relatively high values of τ are related directly to surfactant diffusion.

Diffusion-controlled adsorption has previously been studied (Ferri and Stebe, 2000). We consider its potential role in wetting. Immediately after the formation of an area of surface (interface) in a surfactant solution, surfactant adsorbs leading to depletion of the local (subsurface) concentration. Surfactant diffuses from the (nearby) bulk to supply the region (Chang and Franses, 1995, Miller et al., 1994). We may find a characteristic distance for this diffusion from the following simple argument.

The adsorbed mass of surfactant over a surface area, δA, is given by $C_\infty \delta A$, where C_∞ is the equilibrium surface concentration ($C_{L\infty}$ or $C_{SL\infty}$, depending on the surface/interface in question). This mass of surfactant would be found in a volume, $h\delta A$, immediately below the surface, where it may be expressed as $Bh\delta A$, where B is the bulk concentration. From a simple mass balance, we obtain the characteristic depth, *h*:

$$h \approx \frac{C_\infty}{B} \tag{8.27}.$$

Having obtained this characteristic diffusion depth, *h*, we may infer a characteristic diffusion time which we shall refer to here as τ_D [*cf.* $t_{diffusion}$ in equation (8.1)], assuming that it is essentially the surfactant contained within depth *h*, or volume $h\delta A$, which migrates to the surface. With a diffusion coefficient *D* for the surfactant in the solution, we have:

$$\tau_D \approx \frac{h^2}{D} \approx \frac{C_\infty^2}{DB^2} \tag{8.28}.$$

The value of *D* has been estimated as $\leq 10^{-10}$ m^2s^{-1} for the present molecules, which is in agreement with previously reported values (Svitova et al., 1996, Rosen, 1989, Cazabat, 1994).

If the final stage of wetting is diffusion-controlled, we may suspect a scaling law of the form $\tau_D \sim B^{-2}$, and that $\tau_D \equiv \tau$ in Tables 8.2 and 8.3, τ being the experimental time constant for final wetting. Treating *B* as the independent variable, in Figure 8.6 we present the relationship $\tau^{-1/2}$ *vs.* B for the surfactant solutions of various concentrations on the solids studied. As can be seen, using both data for r and θ, there is a clear increase in $\tau^{-1/2}$ with *B*, and the relation is acceptably linear, in agreement with equation (8.28), tending to confirm our hypothesis of diffusion-

controlled wetting. Applying linear regression analysis to both r and θ data, we obtain the following relations, respectively for Cytop® and Teflon® separately and also together, where R is the correlation coefficient:

$$\tau^{-1/2}(s^{-1}) = 0.4 + 6x10^{5}\,B(mole\ cm^{-3}) \qquad R = 0.99 \qquad (8.29a),$$

$$\tau^{-1/2}(s^{-1}) = 0.9 + 2.9x10^{5}\,B(mole\ cm^{-3}) \qquad R = 0.89 \qquad (8.29b),$$

$$\tau^{-1/2}(s^{-1}) = 0.65 + 4.4x10^{5}\,B(mole\ cm^{-3}) \qquad R = 0.89 \qquad (8.29c).$$

The fact that these lines do not pass by the origin is perhaps to be expected, since the relationship will finally break down at sufficiently low concentrations: $\tau = \infty$ for B = 0 is unreasonable! (As $B \to 0$, a different regime will be encountered since capillary wetting without diffusion will start to dominate.) It is probable that equations (8.29a) and (8.29b) should be taken separately, rather than combined as in (8.29c), since diffusion both to a surface and an interface are involved, the latter being different for the two cases. Notwithstanding, orders of magnitudes are the same, and this is really all we can expect using this scaling approach.

The mechanism by which superspreaders act and improve wetting efficiency is still not entirely understood, but considering equation (8.28), we see that the pre-factor of the proposed scaling law depends both on C_{∞} and on D. Accepting that D will probably be similar for superspreaders and for standard surfactants, it is worth considering the term C_{∞}, which appears as C_{∞}^{2}. This equilibrium surface concentration is likely to be related to the packing density of surfactant molecules at the surface or interface in question.

Judging by the form of the trisiloxane molecule, it is likely that the ‘T’ head adsorbs at the liquid surface, or interface, leaving the hydrophilic tail behind, immersed in the bulk. It is difficult to estimate the area covered by the ‘T’ head with any precision, but a reasonable idea can be gained by considering it to be 8 bond lengths across and 2 wide, giving a surface area of *ca*. 0.7 nm^2 (He et al., 1993). This will compare to a

standard surfactant presenting a hydrophobic group in the range of *ca*. 0.3-0.5 nm^2 (Kunieda et al., 1998, Rosen et al., 1982). Equilibrium surface concentration, C_∞, will therefore be considerably *smaller* for the 'T' shaped molecule. Given that τ_D depends on C_∞^2, such a difference in the ratio of surface areas could easily lead to a *ca*. 2-fold or greater difference in molecular *number* (or molar) surface density, and thus characteristic adsorption time, τ_D, for a given bulk concentration, *B*. Even if the kinetics of adsorption is similar in the two cases, the fact that a considerably lower number of adsorbed molecules is needed at the interface for saturation with the superspreader means that a shorter characteristic diffusion time and faster adsorption result. This more rapid, diffusion-controlled adsorption in the case of a superspreader has direct impact on the wetting kinetics. The attribution of the efficiency of superspreaders to the 'T' shaped molecule is not new (Kumar et al., 2003) , but we believe that the above explanation is.

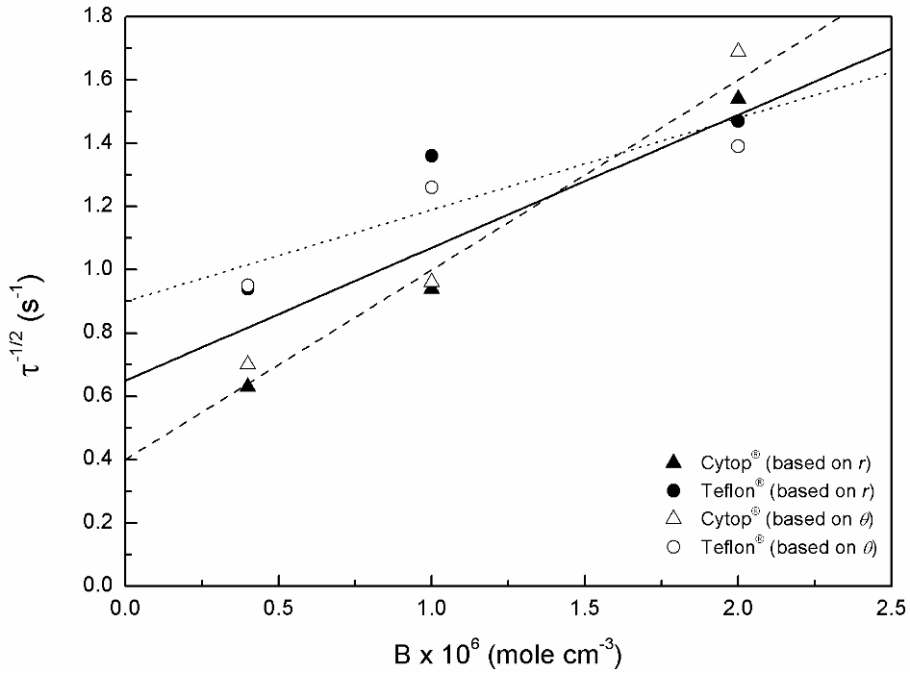


Figure 8.7 Inverse square root of time constant, $\tau^{-1/2}$, for final stage of wetting *vs* surfactant bulk concentration, *B*. Linear trends on the graph: Cytop® - dashed line, Teflon® - dotted line and combined model - solid line.

We shall attempt to consider this aspect semi-quantitatively. Equation (8.28) is written in the form:

$$C_\infty \approx B\sqrt{D\tau_D} \qquad (8.30).$$

The effect is minimal in the following, but since the lower values shown in Figure 8.6 are more likely to be 'perturbed' by purely capillary effects, we consider $B = 2x10^{-6}$ mole cm^{-3} (or 0.125 wt % surfactant), and the corresponding value of $\tau_D \approx 0.4$ second. From above, we take $D \leq 10^{-10}$ m^{2}s^{-1}. This leads to $C_\infty \approx$ 1.3 x 10^{-9} mole cm^{-2}. Multiplying by Avogadro's number, $N_o \approx 6x10^{23}$, we find a number concentration of surface, surfactant molecules at equilibrium of *ca*. $7.5x10^{14}$ molecules cm^{-2}, equivalent to *ca*.$1.3x10^{-15}$ cm^2 molecule^{-1}, or 0.13 nm^2 molecule^{-1}. Clearly we cannot consider this calculation to give an *exact* value of surface coverage by a 'T' head of the surfactant, since it is based on scaling arguments and an uncertain, probably overestimated, value of the diffusion coefficient, *D*. Nevertheless, the agreement with the simple estimate given above, based on molecular dimensions, tends to corroborate the basic explanation presented here to explain both the mechanism of diffusion-controlled wetting and a possible reason for the improved efficacy of superspreaders, *viz*. that the reduced equilibrium number of surfactant molecules at the surface effectively leads to more rapid adsorption and wetting.

8.4 Conclusion

A review of wetting exponents reported in the literature revealed the important role of hydrophobicity of the substrate in the wetting process and suggested the need for a superior model to describe wetting and explain its underlying mechanisms. A theoretical model was developed in order to illustrate dynamic wetting behaviour of commercial superspreaders on moderately hydrophobic substrates. Surfactant diffusion is considered to be the key factor for wetting of concentrated trisiloxane solutions. This has been substantiated by an approximate theory of the final wetting stage. We have confirmed that surface and interfacial tension gradients, which are direct a consequence of difference in concentration between the bulk and the subsurface, decay exponentially due to surfactant diffusion, which we believe is the limiting step in wetting. An appropriate diffusion mechanism has been proposed and the 'motor' for trisiloxane wetting has been defined with two essential terms, which govern the overall wetting dynamics.

Both decrease in contact angle and increase of drop radius over time exhibited exponential behaviour. Semi-empirical equations proposed in this work may be used for simple and easy prediction of the evolution of the wetting parameters. Furthermore, it can be used to determine the final wetting performance of commercial trisiloxane products when mixed with water and estimate their effectiveness on surfaces of varying hydrophobicity. However, further experimental investigation is necessary on a number of substrates, especially on those with higher hydrophobicity in order to expose fully the nature of the coefficients. Nevertheless, we believe that the presented work is a significant step forward to successful revelation of poorly understood trisiloxane wetting phenomenon.

8.5 References

Cazabat, F. T. a. A.-M. (1994) *EPL (Europhysics Letters),* **25,** 205.

Chang, C.-H. and Franses, E. I. (1995) *Colloids and Surfaces A: Physicochemical and Engineering Aspects,* **100,** 1-45.

De Gennes, P. G. (1985) *Reviews of Modern Physics,* **57,** 827.

De Ruijter, M. J., De Coninck, J. and Oshanin, G. (1999) *Langmuir,* **15,** 2209-2216.

Dutschk, V., Sabbatovskiy, K. G., Stolz, M., Grundke, K. and Rudoy, V. M. (2003) *Journal of Colloid and Interface Science,* **267,** 456-462.

Ferri, J. K. and Stebe, K. J. (2000) *Advances in Colloid and Interface Science,* **85,** 61-97.

He, M., Hill, R. M., Lin, Z., Scriven, L. E. and Davis, H. T. (1993) *The Journal of Physical Chemistry,* **97,** 8820-8834.

Ivanova, N., Starov, V., Johnson, D., Hilal, N. and Rubio, R. (2009) *Langmuir,* **25,** 3564-3570.

Ivanova, N., Starov, V., Rubio, R., Ritacco, H., Hilal, N. and Johnson, D. (2010) *Colloids and Surfaces A: Physicochemical and Engineering Aspects,* **354,** 143-148.

Kumar, N., Couzis, A. and Maldarelli, C. (2003) *Journal of Colloid and Interface Science,* **267,** 272-285.

Kunieda, H., Taoka, H., Iwanaga, T. and Harashima, A. (1998) *Langmuir,* **14,** 5113-5120.

Lee, K. S., Ivanova, N., Starov, V. M., Hilal, N. and Dutschk, V. (2008) *Advances in Colloid and Interface Science,* **144,** 54-65.

Lee, K. S. and Starov, V. M. (2007) *Journal of Colloid and Interface Science,* **314,** 631-642.

Marmur, A. (1983) *Advances in Colloid and Interface Science,* **19,** 75-102.

Miller, R., Joos, P. and Fainerman, V. B. (1994) *Advances in Colloid and Interface Science,* **49,** 249-302.

Nikolov, A. D., Wasan, D. T., Chengara, A., Koczo, K., Policello, G. A. and Kolossvary, I. (2002) *Advances in Colloid and Interface Science,* **96,** 325-338.

Radulovic, J., Sefiane, K. and Shanahan, M. E. R. (2009) *Journal of Colloid and Interface Science,* **332,** 497-504.

Rafai, S., Sarker, D., Bergeron, V., Meunier, J. and Bonn, D. (2002) *Langmuir,* **18,** 10486-10488.

Rosen, M. J. (1989) *Surfactants and Interfacial Phenomena,* John Wiley & Sons, Inc, New York.

Rosen, M. J., Cohen, A. W., Dahanayake, M. and Hua, X. Y. (1982) *The Journal of Physical Chemistry,* **86,** 541-545.

Rosen, M. J. and Song, L. D. (1996) *Langmuir,* **12,** 4945-4949.

Summ, B. D., Yushchenko, V. S. and Shchukin, E. D. (1987) *Colloids and Surfaces,* **27,** 43-55.

Svitova, T., Hoffmann, H. and Hill, R. M. (1996) *Langmuir,* **12,** 1712-1721.

von Bahr, M., Tiberg, F. and Yaminsky, V. (2001) *Colloids and Surfaces A: Physicochemical and Engineering Aspects,* **193,** 85-96.

Zhang, Y., Zhang, G. and Han, F. (2006) *Colloids and Surfaces A: Physicochemical and Engineering Aspects,* **276,** 100-106.

Chapter 9 : Capillary Rise of Trisiloxanes

9.1 Capillary Action of Surfactant Solutions

Capillary action is the base of operation of numerous biological and industrial processes. The phenomenon of capillarity is found everywhere; from transport of fluids in plants and through the soil to utilizations in oil recovery and ink printing. Understanding the theory behind capillarity has allowed designing highly efficient engineering applications in the last decades. This is the main reason vast interest in this remarkable, yet elementary, phenomenon has not faded for almost a century. Early formulation by Washburn (Washburn, 1921) has been successfully employed for years and was often used as a foundation for more complex models. Notwithstanding the geniality of his equation, its applicability has certain limitations. The main drawback of Washburn's equation is taking solely viscous forces in consideration. In the subsequent model Bosanquet (Bosanquet, 1923) included inertial effects, while Quéré (Quéré, 1997) introduced more suitable model for the low viscosity liquids. The importance of the change of the dynamic contact angle was also revealed (Martic et al., 2002). While Washburn's equation was found to be suitable for modeling imbibition of pure liquids (Labajos-Broncano et al., 2004), in recent studies (Fries and Dreyer, 2008) attempts have been made to reveal the dominant force in different stages during the capillary rise.

The capillary phenomenon evidently becomes more complex when surfactant solutions are employed. Numerous efforts have been made to explain and quantify behaviour of the surfactants systems in thin capillaries and to model the observed discrepancies from Washburn equation (Tiberg et al., 2002, Churaev et al., 1981, Churaev and Zorin, 1995, Starov et al., 2004, Starov, 2004a, Starov, 2004b, Zhmud et al., 2000). In (Starov et al., 2004, Starov, 2004b, Starov, 2004a, Churaev et al., 1981) it was shown that both the bulk and the surface diffusion of surfactant molecules play crucial role and the adsorption of surfactant molecules in front of the moving meniscus was suggested as the probable mechanism. Starov (Starov, 2004b) introduced three penetration mechanisms of surfactant solutions into hydrophobised capillaries depending on the overall surfactant concentration. At high concentrations

solution penetrates faster into the capillary; at lower concentrations penetration rates are much lower and process is controlled by the reduced surfactant concentration near the meniscus, while at very low concentrations the diffusion mechanism of penetration takes place. In (Tiberg et al., 2002, Zhmud et al., 2000) authors investigated capillary rise of C_nE_6 surfactants and confirmed Washburn's relation was valid only for the initial period, while the overall time dependence of the liquid rise indicates a diffusion-controlled process. However, capillary rise of superspreaders is practically an unexplored topic. To the best of our knowledge no comprehensive experimental or theoretical investigation of capillary action of trisiloxanes has been carried out so far. We have looked into this interesting phenomenon and provided thorough explanation for the observed behaviour of moderately concentrated trisiloxane solutions in capillaries. Our model recognizes both diffusion and adsorption as important factors, yet emphasises trisiloxane-specific interfacial and surface tension time-dependencies, and consequent specific diffusion mechanism, as essential parameters.

9.2 Theoretical Model

Overall balance of forces acting on a noncompressible liquid in a cylindrical capillary may be noted as

$$\rho\left[h\frac{d^2h}{dt^2}+\left(\frac{dh}{dt}\right)^2\right]=\frac{2}{R}\gamma\cos\theta-\frac{8}{R^2}\eta h\frac{dh}{dt}-\rho gh \tag{9.1}$$

where ρ is the density, η is the viscosity, γ is surface tension, θ is the contact angle of the liquid, h is the height of the liquid in the capillary, R is the radius of the capillary tube and g is the acceleration of gravity. The term of the left represents inertial resistance to the flow, while terms on the right are capillary driving force, viscous resistance and change in potential energy, respectively. Starting from the Eq. 9.1,

Washburn (Washburn, 1921) has balanced gravitational and capillary effects at the steady state and obtained an expression for the stationary height of the liquid:

$$h_{\infty} = \frac{2\gamma \cos\theta}{\rho g r} \tag{9.2}$$

By neglecting viscous and inertial contributions a well-known time-dependence of the capillary rise, $h \propto \sqrt{t}$, is obtained, which proved to be the suitable model for pure liquids and very diluted conventional surfactant solutions (Churaev and Zorin, 1995, Starov et al., 2004). For portraying capillary action of more concentrated surfactant solutions a more complex model was necessary.

Starting from Poiseuille's flow, the velocity gradient is

$$v(r) = a\left(r^2 - R^2\right) \tag{9.3}$$

and the advance speed of the liquid front is

$$U = \int_0^R \frac{2\pi r v(r)}{\pi R^2} dr = \frac{-aR^2}{2} \tag{9.4}$$

with *a* being a coefficient. Let us rewrite Equation 9.1 in a more general form (inertial effects assumed to be negligible):

$$\dot{W} = \dot{D} + \frac{d(PE)}{dt} \tag{9.5}.$$

The term on the left is the work done by the capillary force:

$$\dot{W} = 2\pi R \Delta\gamma U \tag{9.6}$$

with $\Delta\gamma = \gamma_S - \gamma_{SL} = \gamma_{LV}\cos\theta$ (Young's equation). Energy dissipation during flow comes from viscous resistance of the liquid and by combining Equations 9.3 and 9.4 we get:

$$\dot{D} = \eta\int_V \left(\frac{\partial v}{\partial r}\right)^2 dV = 4\eta h a^2 \int_V 2\pi r^3 dr = 8\pi\eta h U^2 \tag{9.7}$$

Gravitational effects may be expressed as

$$\frac{d(PE)}{dt} = \pi R^2 h\rho g U \tag{9.8}$$

Substituting the above expressions in Equation 9.5 we get the time dependence of the height of the liquid:

$$U = \frac{dh}{dt} = \frac{R\Delta\gamma}{4\eta h} - \frac{R^2\rho g}{8\eta} \tag{9.9}$$

For $t \to \infty; h = h_\infty$ and under classic conditions ($\Delta\gamma = \gamma_{LV}\cos\theta$) this gives standard capillary rise equation (Equation 9.2). Here we introduce particularity of superspreader solutions: an exponential time-dependence of the interfacial tension (surface tension of the liquid and the contact angle exhibit the same behaviour which is discussed in Chapter 8):

$$\gamma_{SL}(t) = \gamma_{SL\infty} + (\gamma_{SLo} - \gamma_{SL\infty})\exp(-t/\tau) \tag{9.10}$$

This allows us to write

$$\Delta\gamma(t) = (\gamma_s - \gamma_{SL\infty}) + (\gamma_{SLo} - \gamma_{SL\infty})\exp(-t/\tau) \tag{9.11}$$

The first term may be considered as constant since the surface energy of the glass capillary is not changing, $\Delta\gamma_\infty = \gamma_s - \gamma_{SL\infty}$ and the second term may be defined as $\delta\gamma = \gamma_{SLo} - \gamma_{SL\infty}$. Once capillary tube gets in contact with surfactant solution, surfactant molecules quickly migrate onto the bare surface of the tube where they adsorb at very short time scale. However, this dynamics, as will be shown, is typical only for the initial stage. Surfactants, having adsorbed, remain adhering to the tube wall and further uncovered sections need more surfactant to cover the surface. As meniscus advances, newly created *s-l* surface is devoid of surfactants. This initiates the diffusion, which is the time limiting step; surfactant diffuses to the interface and adsorbs later. By combining Equations 9.9 and 9.11 we get

$$U = \frac{dh}{dt} = \frac{R}{4\eta h}\left[\Delta\gamma_\infty - \delta\gamma\exp\left(-t/\tau\right)\right] - \frac{R\Delta\gamma_\infty}{4\eta h_\infty} \tag{9.12}$$

which may be rewritten as

$$\frac{dh}{dt} = A\left\{\frac{1}{h}\left[1 - \frac{\delta\gamma}{\Delta\gamma_\infty}\exp\left(-t/\tau\right)\right] - \frac{1}{h_\infty}\right\} \tag{9.13}$$

with coefficient $A = \frac{R\Delta\gamma_\infty}{4\eta}$. If gravity term is negligible $\left(h << h_\infty\right)$, Equation 9.13 can be easily solved with boundary conditions $t \to 0; h = 0$ giving

$$h^2 \approx 2A\left\{t + \chi\tau\left[\exp\left(-t/\tau\right) - 1\right]\right\} \tag{9.14}$$

where $\chi = \delta\gamma/\Delta\gamma_\infty$. This implies adsorption time scale starts at capillary rise origin, which may be valid only for the initial stage. At later stages adsorption may not be taken as function of the advance speed *U*.

The effective change of $\Delta\gamma$ is near the triple line governed by diffusion (Figure 9.1). Some diffusion processes still take place well behind the triple line, but this should

not affect the capillary rise (Song et al., 2006). Let us introduce ε as effective range of capillary forces, then local time of the capillary rise over ε is $\tilde{t} = \int_B^A \frac{dx}{U(x)} = \int_{h(B)}^{h(A)} \frac{dh'}{U(h')}$ allowing the variation of U. Equation 9.13 then becomes

$$\frac{dh}{dt} = A\left\{\frac{1}{h}\left[1-\chi\exp\left(\frac{-1}{\tau}\int_0^{\varepsilon}\frac{dx}{U(x)}\right)\right]-\frac{1}{h_{\infty}}\right\} \tag{9.15}$$

Provided ε is small $\int_0^{\varepsilon}\frac{dx}{U(x)} \approx \frac{\varepsilon}{U(h)} \equiv \frac{\varepsilon}{U(t)}$ this becomes

$$U = A\left\{\frac{1}{h}\left[1-\chi\exp\left(\frac{-\varepsilon}{\tau U}\right)\right]-\frac{1}{h_{\infty}}\right\} \tag{9.16}$$

Reasonable estimate of the effective range of the capillary forces, ε, is in range of hundreds of nm (Shanahan et al., 1998, Yaminsky, 1997) allowing us to simplify the above equation using $U >> \frac{\varepsilon}{\tau}$:

$$U \approx A\left\{\frac{(1-\chi)}{h}+\frac{\chi\varepsilon}{\tau U h}-\frac{1}{h_{\infty}}\right\} \tag{9.17}$$

Equation 9.17 cannot be solved analytically. Let us consider two limiting cases:

(i) $h << h_{\infty}$: For small rise of the liquid in the capillary, $h \approx 0$, U is high. Having that in mind, it is safe to assume

$$U \approx A\frac{(1-\chi)}{h} \Rightarrow t \approx \frac{h^2}{2A(1-\chi)} \approx \frac{2\eta h}{R(\Delta\gamma_{\infty}-\delta\gamma)} \tag{9.18}$$

Since $\Delta\gamma_\infty - \delta\gamma$ is the effective value of $\Delta\gamma$ *before* significant adsorption, this is a possible method to estimate the 'initial' value of $\gamma_S - \gamma_{SLo}$. Hence, the general trend, $h \propto \sqrt{t}$, typical for the initial stage is conserved.

(ii) $h \approx h_\infty$: In this stage U is expected to be very small, hence $U \to 0; \exp\left(\frac{-\varepsilon}{\tau U}\right) \to 0$. This leads us to the classic solution:

$$h(t) = h_\infty - k\exp\left(\frac{-At}{h_\infty^2}\right) \tag{9.19}$$

where k is pre-exponential factor whose physical meaning may be understood from the initial conditions $t \to 0; h = h_o$. Here we can introduce $\tau = h_\infty^2 / A = 4\eta h_\infty^2 / R\Delta\gamma_\infty$ as the time constant of the exponential capillary rise of the liquid and whose value clearly depends on the properties of the trisiloxane solution and its effective wetting ability.

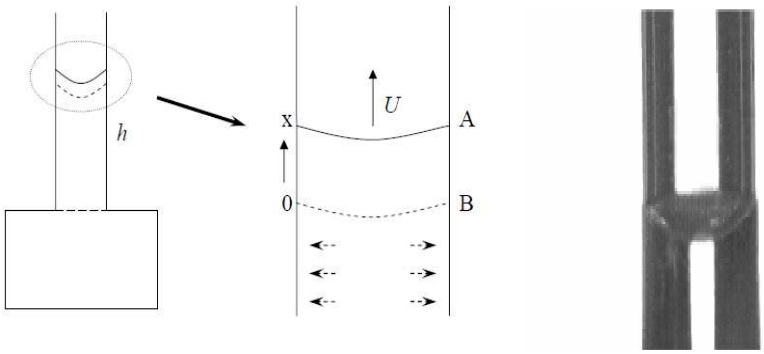


Figure 9.1 Capillary rise of trisiloxane solutions with diffusion to the subsurface as the limiting step and subsequent adsorption at the interface.

9.3 Superspreaders in Capillaries

Four specific concentrations of superspreader Silwet® L-77 were tested: 0.00625 wt %, 0.0125 wt %, 0.025 wt % and 0.1 wt %. Surfactant concentrations were carefully chosen; for the lowest one, 0.00625 wt %, can be safely presumed to be below theoretical CMC (and CAC), which is believed to be 0.0125 wt %; the critical wetting concentration (CWC) of 0.025 wt % and the highest one, 0.1 wt % (4 CWC). Solutions were brought in contact with cleaned borosilicate glass capillaries with internal diameter of 1.63 mm and change in height of the liquid was monitored until equilibrium was reached. Rise of various concentrations of aqueous trisiloxane solutions are presented in Figure 9.2.

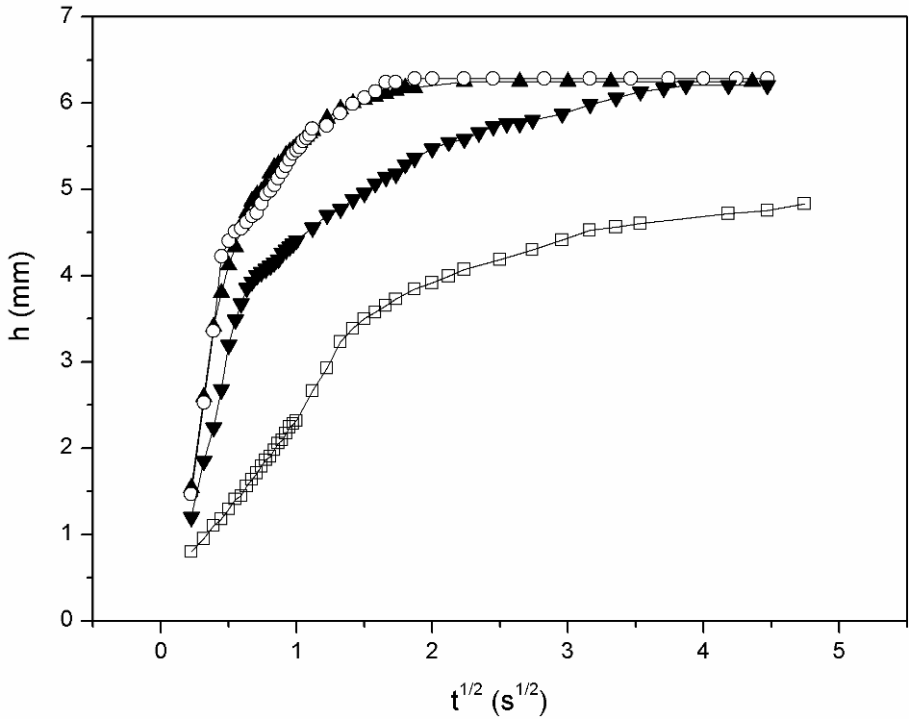


Figure 9.2 Capillary rise dynamics of trisiloxane solutions in glass capillaries. (□), 0.00625 wt %; (▼) 0.0125 wt %; (○), 0.025 wt %; (▲), 0.1 wt %.

Solutions of concentrations equal and above CAC have risen more and needed shorter time to reach equilibrium. Observed behaviour was very different from that a conventional surfactant solutions exhibit (Tiberg et al., 2002, Zhmud et al., 2000). The proportionality of the height of the liquid in the capillary with $\sqrt{t}$ is the property only of the early stage of the capillary action. Advance speed is the highest in the beginning since surfactant molecules instantly adsorb at the bare *s-l* interface, allowing liquid front to advance further up the capillary tube. This is a similarity with other surfactant types: the 'initial' *s-l* interface gets quickly saturated with surfactants (at sufficiently high surfactant concentrations), resulting in jump-like increase of the height of the liquid during the initial step. Hence, this trend is in general agreement with our model (Equation 9.19) for the beginning of the capillary action. The first stage of the capillary rise was found to be ~ 7.5 % of the total time for the majority of the solutions tested (Table 9.1). However, the initial stage was found to be shorter for CAC solution. This can be explained in terms of freely solubilised molecules in the solution being quickly 'spent' on saturation of the initial interface; as soon as more surfactants are needed, disaggregation of micelles takes place and a specific diffusion commences, which alters $\sqrt{t}$ dynamics. Comparison of the heights of the liquid in the capillaries showed similar trends, ~ 60 % of the total height for solutions below CWC and ~ 70 % for solutions above CWC, whose behaviour was undistinguishable. After the initial $h \propto \sqrt{t}$ rise, a distinctive exponential increase, not observed for conventional surfactants, was noticed for the intermediate and final rising times. The final height of the liquid was lower for the solution below CAC, while other three have risen equally. Despite the same equilibrium rise, dynamics of the capillary action was different. Solutions at CWC and above performed identically, following matching dynamics, while the solution at CAC reached the same final height in significantly longer time.

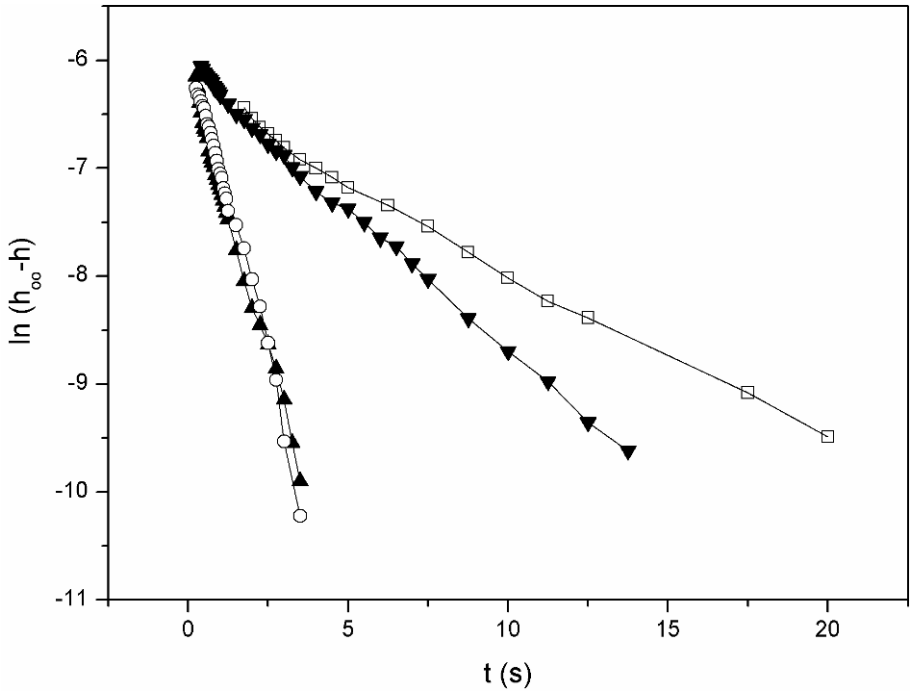


Figure 9.3 Intermediate stage of trisiloxane solutions capillary rise and subsequent exponential relaxation. (□), 0.00625 wt %; (▼) 0.0125 wt %; (○), 0.025 wt %; (▲), 0.1 wt %.

Superspreader solutions of all concentrations seem to exhibit prominent exponential capillary rise. After the sharp initial increase, evident rise of the liquid can be successfully described using an exponential function with typical relaxation towards the end of the process, which is in accordance with our model (Equation 9.19). Values in Table 9.1 confirm the exponential behaviour is the essential characteristic of trisiloxane capillary action, with relatively high R^2 values (0.91-0.99) even when applied on the overall capillary rise, including the initial stage, since exponential behaviour dominates the majority of the capillary process. This proves the importance of diffusion in following (main) stage is unquestionable and this is what gives trisiloxane capillary rise its specific exponential profile. Therefore, values of the time constant and coefficient *k* were determined by fitting Equation 9.19 only to the exponential stage of the capillary rise. Values of pre-exponential factor *k* were found to decrease with increasing concentration, since the 'initial' rise is more prominent for the solutions of higher concentrations; however, this strongly depends on the sensitivity and the capacity of imaging equipment and, therefore, cannot be

taken as reliable parameter. Nevertheless, salient decrease of the time-constant τ with increasing concentration was noticed, showing diffusion to the subsurface/interface plays the crucial role and dictates the overall dynamics. At higher surfactant concentrations there are more freely solubilised molecules in the solution, available to readily adsorb at the interface. However, diffusion to the interface is the limiting step. As the total surfactant concentration increases, so does the number of molecules per unit volume throughout the liquid system, allowing more molecules to reach the subsurface in less time. With more 'dense' packing of surfactants at higher concentration effective path for diffusion of surfactants to the interface is shorter. Hence, the adsorption takes place sooner and the time-constant decreases.

Table 9.1 Estimates of basic parameters of capillary rise.

Concentration		$t_{initial}$	$t_{initial}/t_{total}$	$h_{initial}$	$h_{initial}/h_{total}$	τ	$h_{\infty(calc)}$*
wt %		*(s)*	*(%)*	*(mm)*	*(%)*	*(s)*	*(mm)*
0.00625	*< 0.5 CAC*	*1.5*	*7.5*	*2.93*	*69*	*6.112*	*8.71*
0.0125	*~ CAC*	*0.4*	*2.9*	*3.86*	*70*	*3.775*	*8.34*
0.025	*~ CWC*	*0.25*	*7.2*	*4.39*	*62*	*0.945*	*5.64*
0.1	*~ 4 CWC*	*0.25*	*7.2*	*4.39*	*62*	*0.866*	*5.52*

*$h_{\infty\ (calc)}$ has been calculated using Equation 9.2.

In Figure 9.3, $\ln(h_\infty - h)$ was plotted as a function of time in order to show exponential behaviour as an essential characteristic of trisiloxane capillary action. In order to emphasize the trend, the initial quadratic increase of the liquid height with time was not shown on the graph. For majority of the rise dynamics (> 90 % time) model proposed was satisfactory since after the initial stage 'jump' the height of the liquid in the capillary tube. Moreover, the exponential trend gives reasonable fit due to specific exponential decrease of both interfacial and surface tension of trisiloxane surfactant solutions. After the initial adsorption on very short time scale, liquid penetrates further up in the glass capillary. However, surfactants already adsorbed on the capillary wall would not desorb and follow the liquid front since this is now high free-energy region. Fresh surfactants, needed to adsorb at 'new' *s-l* and *l-g* interfaces, are provided by diffusion from the bulk to the subsurface, which is characterised by ε in out model. Diffusion to the subsurface is the limiting step and follows peculiar

exponential trend, typical for trisiloxanes. Once surfactants have diffused in the vicinity of the interface, adsorption may be considered as instantaneous, and the liquid front may advance. At the same time 'slow' diffusion continues providing more surfactants for adsorption and, consequently, the further rise of the liquid in the tube. This dictates the dynamics until the equilibrium height is reached and ultimately results in an unambiguous exponential trend of the capillary rise.

We also show Washburn's equation cannot be used as suitable model for estimation final height of the trisiloxane solution in thin capillaries. By substituting values of ρ = 1000 kg/m^3, g = 9.81 m/s^2, d = 1.63 mm in Equation 9.2 for the known wetting properties of the solution it should be possible to calculate the expected increase in height. A vast decrease in surface tension (Radulovic et al., 2009, Ivanova et al., 2010) is expected from superspreaders. Glass capillaries used have relatively high surface energy and surfactant solutions with very low surface tension, like trisiloxane solutions, will wet the inner surface of the capillary tube effectively. Wetting angle is known to depend on the advance speed (Hilpert, 2009), but it can be assumed to be rather small in case of trisiloxane wetting of glass, eventually leading to $\theta \approx 0°$ (Siebold et al., 2000). Calculated values were very different from the experimentally determined ones. Not only h_∞ values differed, but also decreased with increasing concentration, as the consequence of the surface tension values decreasing with increasing concentration. For pure liquids, lower surface tension would result in lower wetting angle, thus higher $Cos\ \theta$ leading to overall increase in height of the liquid. However, for trisiloxanes solutions the same wetting angle, close to zero, can be expected at equilibrium. This proves Washburn's relation cannot be used as a precise estimate of the final height of the liquid rise in thin capillaries when more complex fluids are used. Trisiloxane's alteration of the interfacial/surface tension dictates the overall dynamics and the final target of the liquid front.

9.4 Conclusions

Capillary action of trisiloxane solutions of varying concentrations was studied in hydrophilic glass tubes. Due to their unique wetting properties superspreaders have exhibited specific capillary dynamics which have not been previously observed for either pure liquids or surfactant systems studied so far. Initial rise was in accordance with Washburn equation and $h \propto \sqrt{t}$ model, while overall behaviour was successfully modelled using an exponential function. Exponential-like behaviour is the consequence of the specific trisiloxane diffusion dynamic, which acts as the 'brake' for instantaneous adsorption and saturation of interfaces. Model proposed can be a powerful tool for estimating final rise of the liquid containing trisiloxane surfactants. Explanation for observed behaviour was provided, although this extraordinary phenomenon deserves more attention and further extensive research.

9.5 References

Bosanquet, C. H. (1923) *Philosophical Magazine Series 6,* **45,** 525-531.

Churaev, N. V., Martynov, G. A., Starov, V. M. and Zorin, Z. M. (1981) *Colloid & Ploymer Sci,* **259,** 747-752.

Churaev, N. V. and Zorin, Z. M. (1995) *Colloids and Surfaces A: Physicochemical and Engineering Aspects,* **100,** 131-138.

Fries, N. and Dreyer, M. (2008) *Journal of Colloid and Interface Science,* **327,** 125-128.

Hilpert, M. (2009) *Journal of Colloid and Interface Science,* **344,** 198-208.

Ivanova, N., Starov, V., Rubio, R., Ritacco, H., Hilal, N. and Johnson, D. (2010) *Colloids and Surfaces A: Physicochemical and Engineering Aspects,* **354,** 143-148.

Labajos-Broncano, L., Antequera-Barroso, J. A., González-Martín, M. L. and Bruque, J. M. (2004) *Powder Technology,* **148,** 48-52.

Martic, G., Gentner, F., Seveno, D., Coulon, D., De Coninck, J. and Blake, T. D. (2002) *Langmuir,* **18,** 7971-7976.

Quéré, D. (1997) *EPL (Europhysics Letters),* **39,** 533.

Radulovic, J., Sefiane, K. and Shanahan, M. E. R. (2009) *Journal of Colloid and Interface Science,* **332,** 497-504.

Shanahan, M. E. R., Houzelle, M.-C. and Carre, A. (1998) *Langmuir,* **14,** 528-532.

Siebold, A., Nardin, M., Schultz, J., Walliser, A. and Oppliger, M. (2000) *Colloids and Surfaces A: Physicochemical and Engineering Aspects,* **161,** 81-87.

Song, Q., Couzis, A., Somasundaran, P. and Maldarelli, C. (2006) *Colloids and Surfaces A: Physicochemical and Engineering Aspects,* **282-283,** 162-182.

Starov, V. M. (2004a) *Journal of Colloid and Interface Science,* **270,** 180-186.

Starov, V. M. (2004b) *Advances in Colloid and Interface Science,* **111,** 3-27.

Starov, V. M., Zhdanov, S. A. and Velarde, M. G. (2004) *Journal of Colloid and Interface Science,* **273,** 589-595.

Tiberg, F., Zhmud, B., Hallstensson, K. and Von Bahr, M. (2002) *Phys. Chem. Chem. Phys.,* **2,** 5189-5196.

Washburn, E. W. (1921) *Physical Review,* **17,** 273.

Yaminsky, V. V. (1997) *Langmuir,* **13,** 2-7.

Zhmud, B. V., Tiberg, F. and Hallstensson, K. (2000) *Journal of Colloid and Interface Science,* **228,** 263-269.

Chapter 10 : Conclusions and Future Work

10.1 Conclusions

10.1.1 Practical Findings

Wetting and spreading abilities of the commercial superspreader products, Silwet® L-77 and Additive 67®, were investigated experimentally and compared to that of conventional Triton® X-100 surfactant. For Silwet® L-77 superspreader 0.025 wt % was found to be the optimal concentration for enhanced wetting; further increase in surfactant concentration did not affect the overall wetting achievement, only the dynamics. Silwet® L-77 showed superiority on surfaces of varying hydrophobicity, thus attaining lower surface tensions than conventional surfactant solutions of the same concentration. The effect of additives in commercial products on wetting performance was studied by comparing Silwet L-77® and Additive 67®. Presence of additives was important only at very low concentrations, when Additive 67® showed better performance on hydrophobic surfaces. Additionally, superspreading phenomenon was observed on marginally hydrophilic Parylene®, while on hydrophobic surfaces final contact angles were always measurable.

Trisiloxane surfactants, although supreme in water solutions, were severely affected by low pH environment. Somewhat improved wetting was still achievable at lower acid concentrations with very high surfactant concentration, while at higher acid concentrations addition of trisiloxane did not seem to have any effect on wetting. Surface tension measurements of acidified solutions proved that superspreader molecules lost their tendency to adsorb at the *l-g* interface. Lack of the interfacial activity at low pH comes as a consequence of the hydrolysation of the Si-O bonds in the trisiloxane head, leading to the loss of the molecule's diphilic nature. Long-term exposure to water had the same effect on trisiloxane surfactants. Superspreaders gradually lost their wetting ability after a number of days, depending on the total surfactant concentration, as the same hydrolysation mechanism took place due to the autoionisation of water. The phenomenon of trisiloxane ageing in aqueous

environment was quantified and these trends can be used for estimation of the wetting performance of water-aged solutions.

On the other hand, when mixed with diluted acid conventional surfactants exhibited practically the same wetting behaviour as water-based solutions. Therefore, they have been proven to be more suitable for use in the acidic environment, normally found in pesticide and herbicide solutions. Ageing also did not have any effect on the performance of conventional surfactant solutions. Classical nonionic surfactants can be safely premixed with water as the shelf-life of diluted aqueous solutions had no influence on their wetting ability.

Although wetting capabilities of the commercial superspreaders, Additive 67® and Silwet L-77®, were found to be very similar, once mixed with conventional Triton X-100® surfactant their performance started to vary significantly, while exposing the important role of additives in commercial superspreader products. Lacking, or occurrence, of the ideal mixing behaviour at certain concentrations revealed several underlying phenomena: 'slim' Triton X-100® molecules inserting themselves between closely packed trisiloxane molecules adsorbed at the interfaces, steric hindrance in mixed micelle formation at specific concentrations due to dissimilar geometries of the hydrophobic heads of conventional surfactants and superspreader molecules, and possibly different chain lengths, and stabilisation of mixed micelles and enhanced wetting due to the presence of additives. These findings give valuable insight into how to optimise the composition of commercial superspreaders by using conventional surfactants as additives. This would enable improved performance on surfaces of specified hydrophobicity, while allowing significant reduction in price.

10.1.2 Theoretical Contributions

The important role of hydrophobicity of the substrate in the wetting process was revealed through an extensive review of wetting exponents reported in the literature so far. This also exposed the need for a superior model to describe trisiloxane enhanced wetting and explain the complex underlying mechanisms they follow. Our

model considers surfactant diffusion as the key factor for specific trisiloxane wetting dynamics. We have proved that surface and interfacial tension gradients decay exponentially due to surfactant diffusion, which is the limiting step in wetting. An appropriate diffusion mechanism has been proposed and the 'motor' for trisiloxane wetting has been defined with two essential terms, which govern the overall wetting dynamics.

Both decrease in contact angle and increase of drop radius over time exhibited exponential behaviour. Semi-empirical equations proposed may be used for simple and easy prediction of the evolution of the wetting parameters. Furthermore, our model can be used to determine the final wetting performance of commercial trisiloxane products when mixed with water and estimate their effectiveness on surfaces of varying hydrophobicity. Based on the same assumptions, a model for prediction of dynamics and the final height of the capillary rise of superspreaders was also developed.

10.2 Future Work

This thesis is a step forward toward revelation of trisiloxane's interfacial activity. Crucial factors that can severely affect their behaviour have been identified and light have been shed on complex diffusion and adsorption mechanisms they follow. Although I like to believe work presented in this thesis could have a positive influence on current commercial trisiloxane products and, more importantly, on their applications, there are still lots of pieces yet to be found before the puzzle of superspreading is completed. Further research is necessary in order to have a more detailed picture, although this thesis highlights some central points for trisiloxane applications and tackles delicate issue of their limitations.

Most experiments were carried out on nearly ideally flat substrates. Regardless the trisiloxane efficiency on these substrates it is worth investigating how superspreaders would perform on non-ideal substrates. A continuation of investigation of trisiloxane performance should include wetting on 'designed' substrates, such as those with

significant roughness, substrates with real-like defects of simple geometries and/or designed (patterned) substrates of varying hydrophobicity.

Logical continuation of the investigation of the effect of pH on trisiloxane wetting would be examining the performance of superspreaders in a wide range of pH for varying surfactant concentrations. Not only this would allow setting solid boundaries of trisiloxane's usage, but might also provide additional insight in aggregation mechanism in more details. Testing even higher surfactant concentrations at various pH environments and when aged at different times, and perhaps measuring surface tensions daily, could lead to vast improvements in existing uses of siloxane-based products and applications.

Extension of the investigations of binary mixtures containing superspreaders is virtually unlimited. Search for binary surfactant mixtures that exhibit synergistic interactions, and consequently allow exquisite wetting performance, is yet to become a challenging research topic, especially having in mind a number of surfactants that could be possibly mixed with superspreaders. This could lead to introducing several specifically designed products on the world market.

Possible extensions of the investigation of trisiloxane rise in capillaries include tubes of various hydrophobicity, geometry and design. Experimental investigation of imbibition of commercial superspreaders into porous substrates could also be an interesting topic, which would not only additionally reveal the effect of the additives, but could also have immense practical impact, if conducted on widely used porous materials.

Due to extremely widespread use of wetting agents there are infinite possible applications of superspreaders still waiting to be revealed. In this thesis, I tried to fully expose few very practical applications of trisiloxanes, but many are yet to be discovered. New potential appliance for employing trisiloxanes would make an excellent and certainly promising research project I would love to be involved in myself.